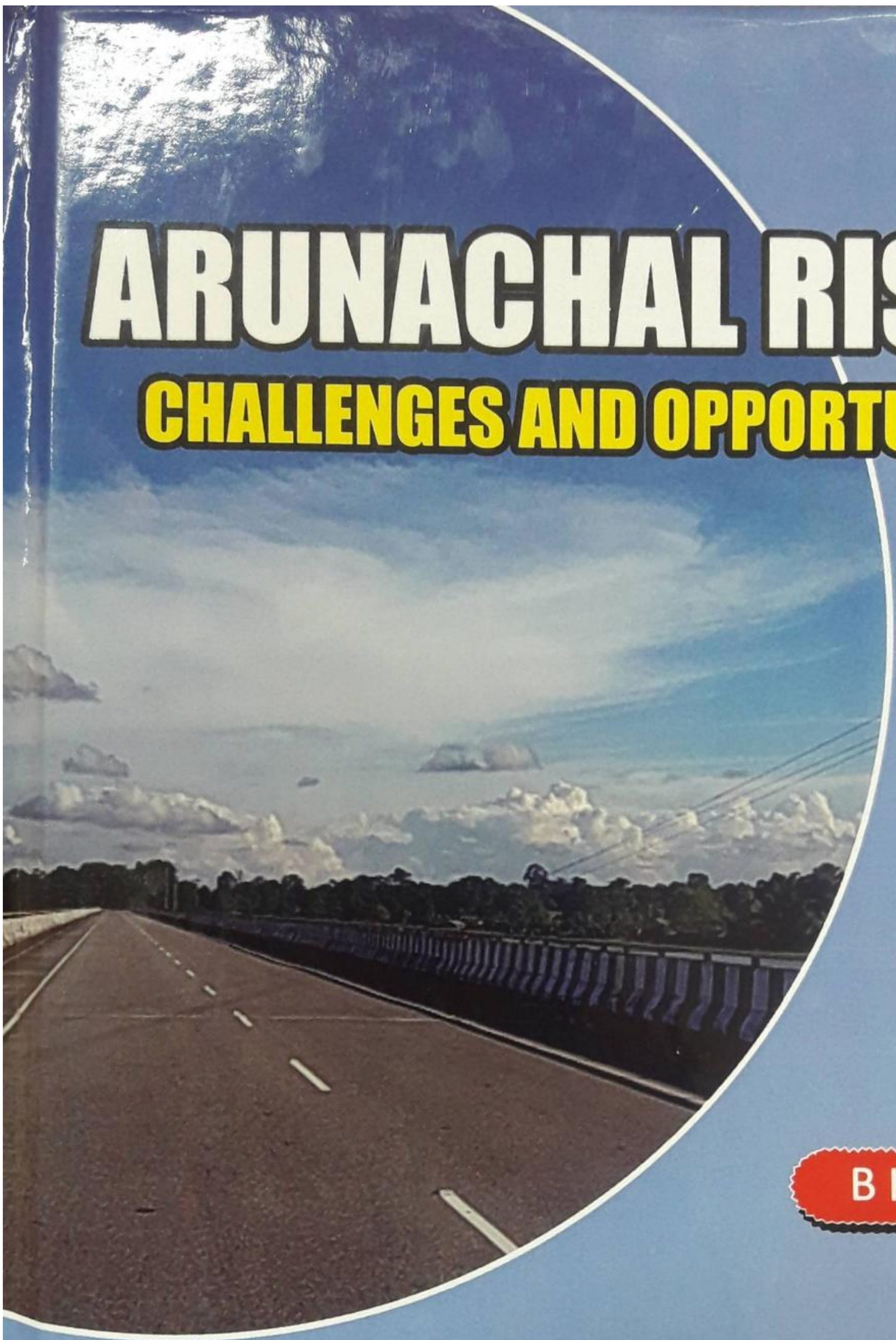
ARUNACHAL RISING:

CHALLENGES AND OPPORTUNITIES



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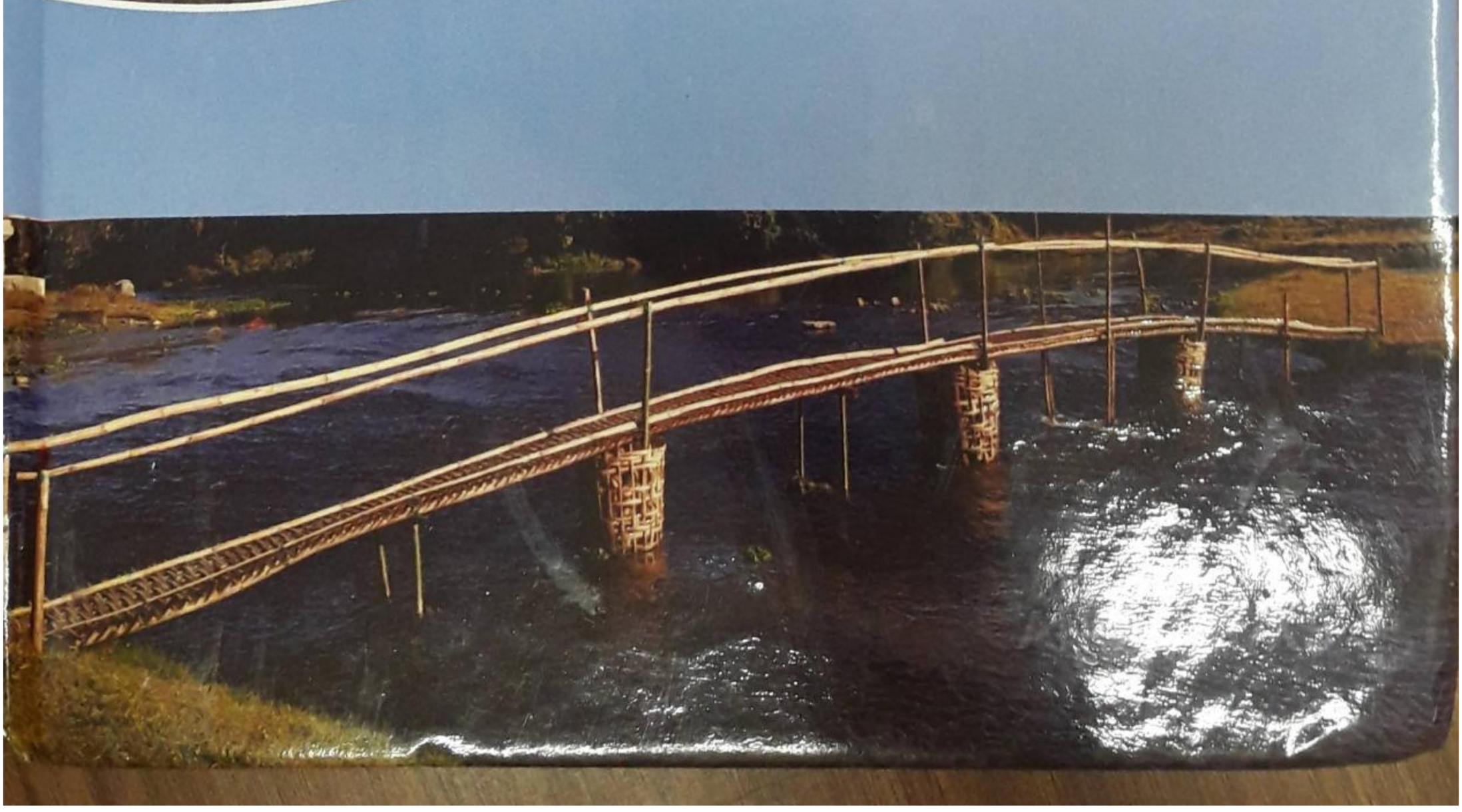

Arunachal Rising : Challenges and Opportunities

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Content

5

A Study of Spiritual Intelligence among the Postgraduate Students of Arunachal Pradesh

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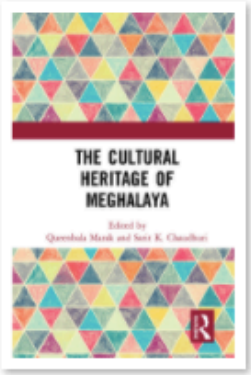
Spirituality and its various aspects have become one of the most interesting topics in today's psychological researches. It open up wide horizons that give profound information about the impact of spiritual forces on human body and mind which in turn clarifies the importance of spirituality in one's life. Studies on spiritual aspects have contributed enormous information about its relationship to mental health and overall health of an individual. Spirituality is considered to be a capacity to know the essence of the existence. Many theorists have considered spirituality as a source of all individual thoughts, feelings, behaviour



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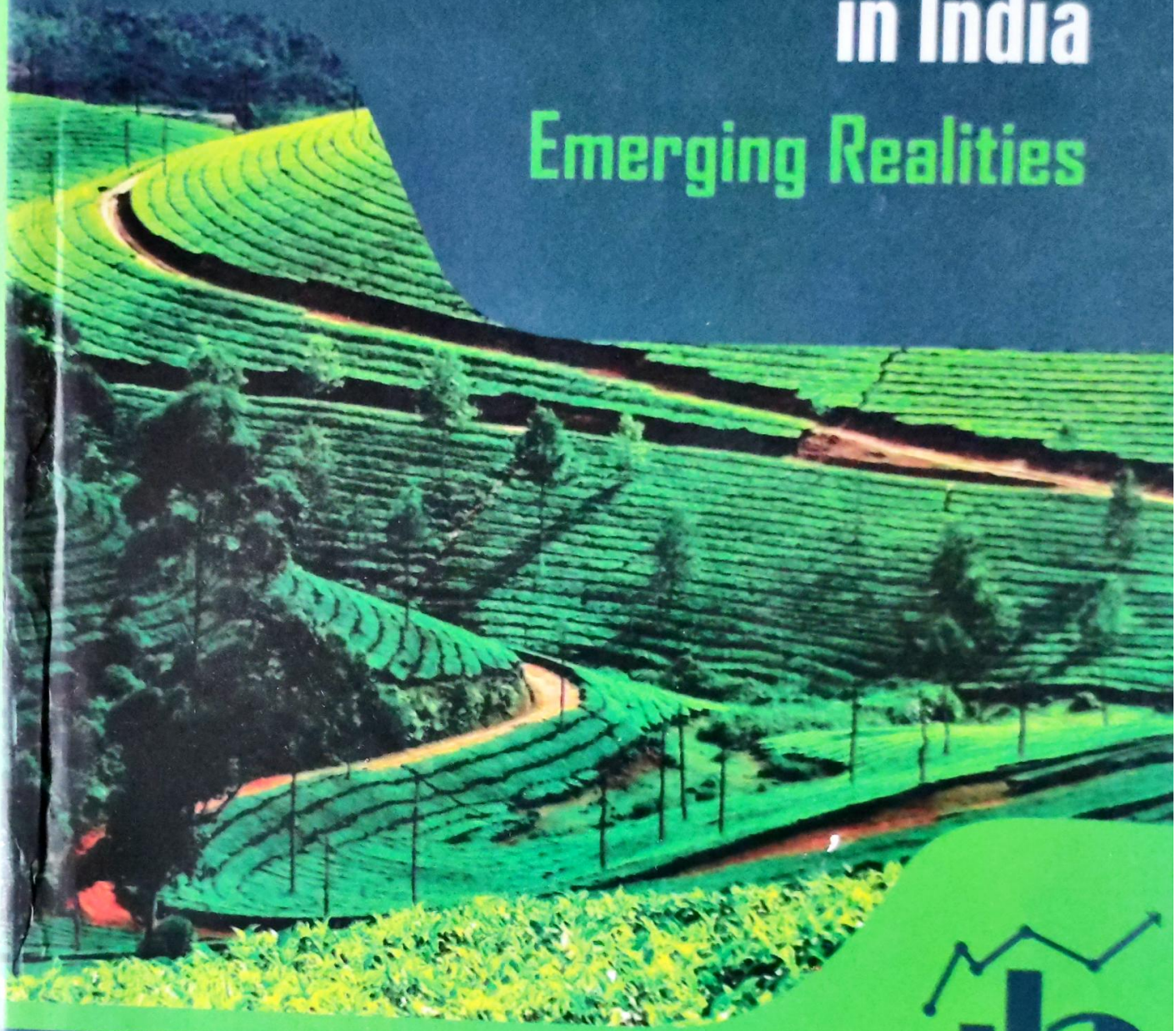

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Contents

E-learning in Higher Education in India: Experiences and Challenges—An Exploratory Study

Kiri Taso and Arindam Chakrabarty

Abstract The world community is committed to achieve 17 goals popularly known as United Nation Sustainable Development Goals (UNSDGs) of which education has been given major thrust that has been earmarked in Goal 4. As a member country, India has also attempted to address the issues of education with highest priority that is envisaged by the responses of the government for drafting New Education Policy in 2019. The government is committed to achieve inclusive education that needs the manifestation of e-Learning platform. Since it is difficult to bring the elephantine population under the ambit of conventional education system, this paper has attempted to explore the experiences and challenges of e-Learning mechanism in the higher education system of India.

Keywords E-Learning · UNSDGs · New Education Policy · Inclusive education · Conventional education

1 Introduction

E-Learning can be defined as an online educational learning process. It can simply be understood as 'Internet-Based Learning'. It is an online learning service through which teaching–learning process is carried out. In other words, e-Learning refers to 'the mode of teaching and learning via Internet and website'. E-Learning is adopted by an institution to let the students learn from home and far distance through online mode which would make the teaching–learning process more approachable and convenient to some extent. E-Learning is primarily the network-enabled practices of skills and information transfer between the online learners and resource providers.

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E-Learning refers to the using of electronic application and processes to learn. 'E-Learning can be in other words understood by means of learning through electronic way by adopting modern means of technological learning. E-Learning can be understood as the network-enabled transfer of skills and knowledge to individual as well as masses. It is opposite to offline and non-electronic means of teaching and learning practices (www.economictimes.indiatimes.com/definition/e-learning). Henceforth, the use of computer–desktop and laptop, mobile and tab and other means to deliver teaching–learning process through the use of Internet source can be simply known as e-Learning. To some extent, we can say online learning (e-Learning) is gradually doing away the traditional learning methods.

Concept of ICT:

Information and Communication Technology (ICT) in the field of education is a significant concept to understand. The various curricular developmental projects have been carried out under the assistance of IITs and NITs. The National Mission on Education initiative by the Government of India is expected to boost the Gross Enrolment Ratio (GER) in Higher Education by 5 percentage (%) points during the Eleven Five Year Plan (2007–12). This Mission has two major components which are (i) Content Generation and (ii) Connectivity—along with a provision to provide devices to institution and learner. Besides that the Mission also seeks to provide computer infrastructure and connectivity to over 18,000 colleges and nearly 400 Departments at Universities and Deemed Universities and Institutions in India for a greater national cause. It also provides interactivity and problem-solving approach which will be addressed through the program called 'Talk to a Teacher' Segment.

2 Electronic Learning or Usage of e-Resources Learning

Massive Open Online Course (MOOC):

MOOC is an online course which committed to provide 'Massive' and 'Open' online learning platform via the web. The MOOCs system of learning begins in the year 2001 at the USA. And it became a trendy approach of learning since 2012 onwards (The New York Times, 18 April 2014).

And the below table shows the students admitted in Coursera enrollees:

Sl. No.	Country/region	Percentage (%) Approx
1.	Russia	2.3
2.	Australia	2.4
3.	Canada	3.5
4.	UK	4.5

(continued)

(continued)

Sl. No.	Country/region	Percentage (%) Approx
5.	Spain	4
6.	India	8.7
7.	Brazil	5.2
8.	USA	27.6
9.	Contribution of the different part of the world	42

Source Coursera Enrolees

SWAYAM

The main goal of the SWAYAM is to deliver quality and reachable educational learning prospect to every needed person specially the underprivileged and unreachable section of society. The SWAYAM actually strives to acts as link for those students who are digitally divided and untouched by e-Learning or Digital Revolution process. The indigenously developed IT platform enables the SWAYAM to propagate all the courses that are being thought by the best teacher in the country and are being made universal access to anyone and at anytime at free of cost.

The programmes and features that offered in SWAYAM are giving education from class 9th to postgraduate n which they offer courses like Science, Engineering, Management, Humanities, Mathematics, Arts and Recreation, Commerce, Language, Education and Library courses, etc., given below:

How to access SWAYAM?

SWAYAM can be accessed through two major ways as follows:

Sl.No.	SWAYAM can be accessed through
1	One can access the SWAYAM portal on the web through https://swayam.gov.in
2	One can also access the SWAYAM mobile apps for—***Android and iOS version***

Source SWAYAM, GOI and Swayam learning portal

Review of Literature

Cox [4], (pp. 85–105) explains the necessity of e-Learning which enhanced our understanding on learning and Information Technology (IT) in teaching and learning process in order to have a clarity and consistency of subject and further highlights that although the young generation has wider access to Information Technology (IT) little is known about this impact on their learning process. There is also a need to balance between the formal and informal uses of e-Learning.

Dewan's [5] study reveals that 80% have computer, 80–67% and 20–33% have no computer. Thus, a better infrastructure is required in institution to provide e-Learning curriculum to the e-Learner.

Rana and Lal [7] highlight that there is need of conventional and holistic approach in educational system which will meet the demands of e-Learners at schools, colleges and universities level. The e-Learning institution with the help of World Wide Web (WWW) via Internet tried its best possibilities to promote distance education, virtual and e-Learning approach by delivering and sharing resources, promoting active e-Learning technologies.

Rosenberg [8] says that e-Learning enables us to understand and deals with different web-based contents for teaching–learning process.

Longmire [6] emphasised that 'an e-Learning approach includes a wide range of digital and computer-based learning mechanism'. He further states that e-Learning content is mainly conveyed via Internet, satellite communication, audiotape and videotape, DVD, CD-ROM and TV and still emerging so-called wireless application protocols (WAP).

Agarwal and Nisa [1] focus on the knowledge process outsourcing sector of India. Authors highlight the scenario which had witnessed the rapid change from 'industrial to knowledge-based economy'. Both also highlight the Skyrme [9] and Stiglitz [10] views on 'how the highly skilled labour force is the key to achieved success in the knowledge-based economy and industry'.

According to Tripathi and Jeevan [11], the paradigm shift in teaching–learning process (traditional to e-Learning) is perhaps due to rapid evolvement made in the field of Information and Communication Technology (ICT).

Ali [2] states that the exponential advent in the field of ICT and Internet has greatly influenced and revolutionised the way the knowledge is broadcasted.

3 Objective of the Study

The paper contains the following objectives:

1. To explore various e-Learning portals operating in India.
2. To explain challenges in implementing e-Learning mechanism for effective teaching dissemination process.

4 Analysis I

Due to the emergence of many well-financed institutions which later link with some of the top universities like Udacity, Coursea and edx, etc., at this period, the year 2012 was regarded as the 'The year of MOOCs' as per The New York Times (2 November 2012).

5 Popular e-Learning Firms/Platforms in India: Indicative List

The emergence of cloud computing technology has highly impacted the Online Education Market in India. The cloud technology with its potential capabilities provides a significant amount of data, information and content at single platforms to e-Learning Companies in India. Due to data saving scope, it is easier for the users and providers to procure, manage access and process the information from anywhere and anytime. Another important reason behind the growth of e-Learning markets trends in India is the rising popularity of big data and learning analytics. The technology enables the companies and institutions to provide online courses to the learners. The e-Learning markets due to its significance potentiality and effective results attract many learners to be aware and opt e-Learning courses. This rising awareness on online learning scope has pushed the growth of online education markets in India. The involvement of Information Communications Technology (ICT) in the field of teaching–learning process has led to the increasing demands of alternative educational approach of learning, which provides significant opportunities for growth of the e-Learning companies in India via digital platform. Thus, it is forecasted that Indian e-Learning markets potentiality will be expanded up to US$18 billion by 2022.

E-Learning Institution in India in 2019:

The emergence of cloud computing technology has highly impacted the Online Education Market in India. Due to data saving scope, it is more easier for the users and providers to procure, manage, access and process the information from anywhere and anytime. Another important reason behind the growth of e-Learning markets trends in India is the rising popularity of big data and learning analytics. The technology enables the companies and institutions to provide online courses to the learners. However, it is forecasted that Indian e-Learning markets potentiality will be expanded up to US$18 billion by 2022 (www.technavio.com).

1. **BYJU'S**: BYJU'S is a learning app founded by Byju Raveendran. In 2019, it has a total net worth of $5.4 billion (Rs. 37,000 crore). This firm has efficiently created a K12 learning smartphone app which offers highly effective, adaptive and active engaging learning programmes. This Edetech app not only provides effective tutoring programme at school level but also efficiently delivers a e-Tutoring to various other competitive exams like IIT-JE, UPSC, CAT and GRE, etc.
2. **IGNOU**: IGNOU stands for *Indira Gandhi National Open University* a Central University which is located at Maiden Garhi, New Delhi. It was established in the year 1985. It has a total enrolment of over 4 million students with 67 centres across the country, the reason why it is regarded as world's largest university. The university serves under the motto of—*The People's University*. IGNOU was founded to serve universal and accessible quality higher educational opportunities in India through the means of *Distance and Open Education*. IGNOU offers 226 academic programs like Diploma, Degree and Certificate courses such as

School of Social Science, Sciences, Education, Engineering and Technology, Management Studies, Computer and Information Sciences, Health Sciences, Law, Journalism and New Media Studies, Vocational Education and Training, Foreign Languages and Performing and Visual Arts, etc.

3. **Dexler Education** (2001): It is located in Bangalore (India). The Dexler Education primarily deals with digital education and consultative services in educational sector. The company provides industry-based e-Learning education solution for corporate learning, talent and faculty management and enhances easier mode on e-Learning. Along with its inventive and skilled e-Learning tactics in delivering quality education to the needy students and organisation, the Dexler Education acquired certain position among the highest e-Learning institution in country.
4. **The Educomp Solution (1994)**: It is in Gurgaon and an Indian-based company. Its aims to replace the traditional way of learning with more advance and smarter way of teaching and learning. Educomp Solutions is ranked among the best e-Learning companies in India. As there is saying—*the numbers speaks*, there are 30 million learners across and 65,000 schools in Educomp Solutions in two decades.
5. National Institute of Information Technology (NIIT-1981): It is situated in Gurugram (India). NIIT provides various kinds of e-Learning courses such as managing, self-learning and instruction training, etc. NIIT is specialised in providing knowledge to certain domains such as corporate, skills and career and schools learning groups. NIIT also offers necessary e-Learning facilities to the deserving and socially challenged and deprived students to certain extent.
6. **Edukart** (2017): It is also listed among the top online educational learning companies in India. Edukart is one of Indian higher education enrolment platform for e-Learner. It is an e-Learning entrance coaching site that provides online learning services to the educational seekers. Edukart also offers admission to certain curriculum such as Diploma and Degree Courses along with Entrance and Certificate, etc. Edukart has linked with some well-recognised educational institution in India like Indian School of Business, National Narsee Monjee Institute of Management Studies-School, etc.
7. **Simplilearn**: It is also one of the top e-Learning platform in San Francisco, California (USA) and Bangalore (India). The Simplilearn also delivered various e-Learning programmes such as cloud computing, digital markets and cyber security course, etc., to the online learner. This institution today achieved successful position among the successful online educational institution in India.
8. **Zeus Learning (ZL)**: It *is* also an online learning institution whose headquarters is at Mumbai (India). It occupies top ninth position among the top online learning institution in India. Zeus Learning offers various programmes to the online learner such as software and apps designing, training and solution for mobile and other technological system, etc.
9. **Meritnation**: It provides live online interactive and tutorial classes to the e-Learning seekers. It is an Edu tech start-up, which is a part or division of Applect Learning Systems based in Delhi (India). **Meritnation** is an online learning

providing institution that delivered various types of e-Learning approach to its e-Learner, so that there could be effective online teaching–learning practices.

10. **Excelsoft**: Excelsoft was founded in the year 2000. Excelsoft provides value courses, product and to cater to the needs and demands of all the key educational sectors like K12 learning system, higher education level, corporate learning, etc.

6 Analysis: II

The e-Learning system is vital for rapid teaching, learning and dissemination process but there are inherent challenges as well. A few key indicative challenges are mentioned below.

(a) Lack of uninterrupted power supply is one of the major issues in the online learning process. Since e-Learning system wholly depends on electricity, there has been frequent interruption in power supply that creates disruption in e-Learning process.
(b) Lack of Internet coverage across the country is another key issue to be addressed in order to provide better and quality digital learning capability of the learner of the country.
(c) Technical issues are yet another matter of concern since the entire process of e-Learning revolves around technology, and if there is technical issue that exists in the learning process, it will definitely hamper the e-Learning process.
(d) Lack of professional skills is another issue need to be redressed, as it requires a well-qualified and skilful professional person in the online education system. If the knowledge providers lack the professional skills, then it will again create problems in such teaching–learning process.
(e) Smooth e-Learning process is hindered by the inherent struggle for adaptability of computer skills. In this type of learning pattern, both the teacher and students need to have well versed in the field of computer technology.
(f) Lack of motivation, i.e. self-motivation is another important matter. Since it lacks face-to-face interactive methods, sometimes students remain unmotivated in their learning process.
(g) Reliability of e-Materials is another important concern, as we do not know the reliable source of materials that are being provided to the students.
(h) Most of the e-Platform is unidirectional. In other words, the learning process in the e-Learning process is one-way learning platform to most often. The learner most often did not get time to have face-to-face contact with the resource person [3].
(i) The e-Learning system also suffers from lack of personal or humanistic touch or human factor in the fields of teaching–learning pedagogy. E-Platforms suffer from real-time interactions, since classes are online in nature with time-specific guidance which makes difficult for the learner to attend the exact schedule classes which is another matter of concern for e-Learner.

(j) Lack of adequate e-Materials is another important issue where the learner may face certain problems. The e-Materials are developed as generic not specific to field of inquiry which lacks the flexibility learning capability or interdisciplinary knowledge of the learner.
(k) Huge initial investment for production, preparation and access of materials at the beginning.

7 Limitation of Study

The paper is developed to explore e-Learning practices in the higher education system of India. Since the e-Learning pattern is in the nascent and formative stage in the country, it is difficult to retrieve longitudinal database in terms of number of users, period of usage, qualitative aspect of e-Learning process, etc. So, this paper essentially suffers from adequate relevant information at this moment. However, the paper has attempted to outline the overview of e-Learning process in Indian higher education system.

8 Conclusion

This study can be regarded as a very foundation work in the domain of e-Learning intervention in Indian higher education system. The study indicates that the e-Learning process has gained momentum over a period of time, and it signifies that both the public and private sectors are contributing to this segment that can achieve the inclusive education model up to the extent of higher education level in India.

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A Novel IoT-Based Approach Towards Diabetes Prediction Using Big Data

Riya Biswas, Souvik Pal, Nguyen Ha Huy Cuong and Arindam Chakrabarty

Abstract Big data is a modern teamster of today's economical world. Data are being digitalized in today's world as imperative judgment is taken by Big data analytics. In our manuscript, we have discussed about Big data analytics in IoT ecosystems and its implications in healthcare. Healthcare is concerned now a days and big data is holding all the supportive hands in IoT-based healthcare systems. In healthcare, we have discussed about Diabetes Mellitus which is a non-communicable disease. This paper deals with the proposed system of diagnosis of diabetes. Hence it is assertive that we do some surveys on how we can manage to handle large data files, technologies are defined and also predictions of diabetes through IOT sensor and management have been discussed.

Keywords Big data · Hadoop · Map reduce · HDFS · Pig · HIVE · HBase · IoT

1 Introduction

In current surroundings data is generating from multiple origin. These data is of multiple diversity. This bulk of enormous data is considered as Big Data. Big data and IoT are the buzz words now days. It is used to express cumbrous bulk of structured and unstructured data. Some characteristics of Big data being discussed [1, 2].

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The amount of data can be blunder, malleable and scalable data which are processed through technologies used called Hadoop, Map Reduce, HIVE, Pig. The production of volume of data is rapidly enlarging every year due to occurrence of newly technologies, accessory and communication [3]. In the modern milestone of smart phones and wearable devices, endless sum of health data folder of patient from different challenges continue featured by healthcare industry [4]. Mostly confusion begin where system process through heterogeneous data sets [5, 6]. In healthcare sector a leading non-communicable disease (NCD) is Diabetes Mellitus. There are basically three stages of type 1 diabetes, type 2 Diabetes, Gestational diabetes. Diabetes is a scheme of metabolic diseases consist of high blood sugar levels concluded lengthy season a numerous operation supported on Internet Of Things been developed for management of diabetes and it composite of physical objects [7, 8]. IOT is mostly a model for interconnecting sensor which does tracking, sensing, processing and diagnosing, coming up with a enclosed device and detector which can link up and also exchange content beyond the internet [9, 10].

In this paper, we are going to discuss literature survey of the related work in the Sect. 2. Section 3 deals with the architecture of the proposed diabetes diagnosis system, proposed algorithm, and sequence diagram of the algorithm.

2 Literature Survey

In this section, we have discussed on literature survey of the background study. Chavan et al. [9] have discussed about Big data is a word which defines massive and convoluted set of data. Some technologies like Hadoop, HDFS, Map Reduce, Pig, Hive, HBase being used. Khan et al. [11] have expressed a proposed data life cycle which utilize employ the technologies and nomenclature of Big data management, investigating and scarceness. Nizam and Hassan [12] have discussed that it is tough to operate with Big data resolving management traditional dataset. Chen et al. [13] have discussed that Initially generic background of Big data is inform then study about the connected technologies i.e. cloud computing, Internet Of Things, data centers and Hadoop. Archenaa and Mary Anita [14] have deliberate about the approach of how we expose newly expose surplus value from the data autogenic by healthcare and government. Prasad et al. [15] have discussed that diabetes is one of the leading non-communicable disease Mellitus. This system will prophesy searching algorithm in Hadoop/Map Reduce. Huzooree et al. [16] has explains that Diabetes Mellitus (DM). The goal of this paper is to ecumenical review centering on recent glucose projection model is declared depending on the rating to performing data analytics in wireless body area in network system. Kumar and Pranavi [17] has discussed that the important function is providing dilution healthcare by modern application such as Big data and cloud. A ecumenical survey is made on diabetes dataset with random forest (RF), SVM, k-NN, CART and LDA algorithms. Joaheer and Nagowah [18] have explained Telemedicine, Electronic Health Records (EHR) and social media. This paper also describes the repung of Big data and also it proposed architecture for

diabetes Mellitus to predict patient with chronic disease in maturius. Saravana kumar et al. [19] have discussed that the unstructured nature of lifecycle from healthcare of Big data This paper analyzing algorithm in Hadoop/Map Reduce is used for prediction of diabetes type, hindrance. Al-Taee et al. [20] has discussed that the self-management of diabetes by IOT based podium. A completely practical model system is created, achieved, point-to-point function is approved successful.

3 Architecture of Proposed Diabetes Diagnosis System

This section describes the architecture of diabetes diagnosis system that analyzes the various Data and initially it accumulated data from numerous devices and it is initially stored in an unstructured or semi-structured format. Initially data should be digitized to stem EHR as well as data are smart devices, research and development SNM data repository which is begin captured by existent technologies and used to redirect those data to centralized database for anatomy. The data are gathered for processing in Hadoop data system then data will be accumulated by apache flume. Apache flume is used here which is a item of hadoop ecosystem. Then the data will be pushed to Hbase by agents for further processing (Fig. 1).

The outputted data moves to HIVE it is a business application running in SQL queries against a hadoop cluster. It uses then map reduce. Map reduce has two tasks

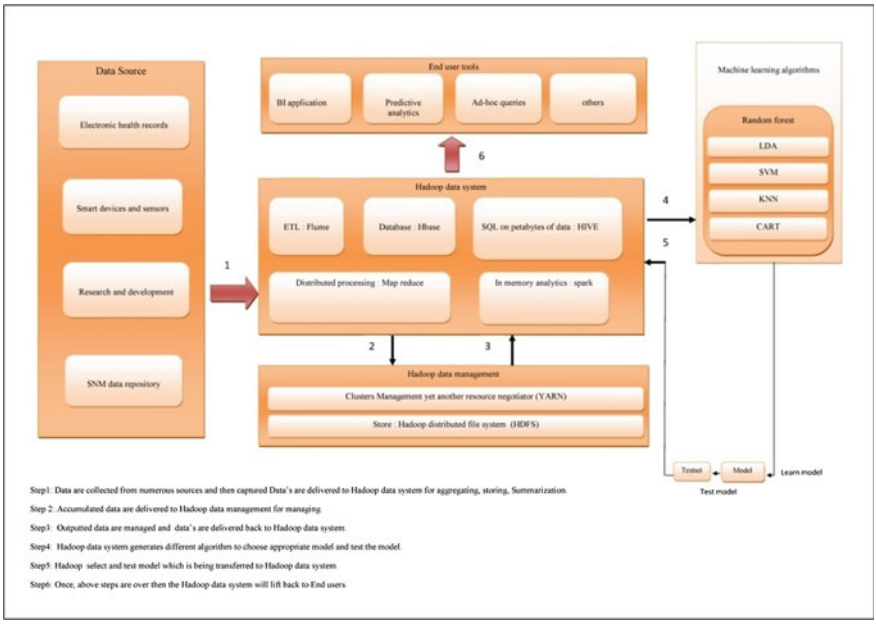

Fig. 1 Architecture for our algorithm

data is splitted and passed into mapping function for produce output values. Next data can use spark which is a frame work that is same as hadoop which provides open-source platforms and can be used by anyone. Then the outputted data are aggregated in hadoop data manager where YARN is used i.e. it is a centralized platform. Then implementing various machine learning algorithms such as RF, LDA, CART and K-NN for prediction it also learn specific data and the test absolute model which will be back to hadoop and hadoop data system will completely send it back to end user tool.

Here it initially identify the course of people tolerate from diabetes registry by working healthcare analytics to big data technology for identifying the diabetes.

3.1 Proposed Algorithm

This section deals with the proposed algorithm of the diabetes diagnosis system.

Step 1: *Initially data assembles from various sources like EHR, smart device and sensors devices and research and development and SNM data respitory.*

Step 2: *Hadoop is a framework which permits for distributed processing of enormous data set. It is a framework which has a capability for stocking and considering data which are prevailing in various machines. It also service map reduce which permits for diving the query into limited chunk and achieve them in co-ordinately.*

Step 3: *Initialized data's from various sources need to be delivered to hadoop data system to process the data where the data's are accumulated by using apache flume, then data moves to HIVE which run SQL queries then data's are place down to map Reduce for summarization. After that spark is used which furnish a open-source platform.*

Step 4: *The processed data's aggregated from hadoop data system need to be managed, so to manage the data are implemented in hadoop data manager where YRAN is used to add new features to the hadoop. It is a centralized platform used for Resource Management.*

Step 5: *The outputted values of managed data are a switched back to hadoop data system.*

Step 6: *The outputted data should be evaluated so Hadoop data system will generate machine learning algorithm.*

Step 7: *Hadoop ensures the appropriate algorithm for the data does evaluated according to their category, from the set of algorithm to determine the appropriate data pattern and lining the data for earning prediction.*

Step 8: *Outputted data tested by Hadoop and draws one specialized model of algorithm and learned the specific model.*

Step 9: *Outputted data are for specific algorithm switch back to hadoop data system.*

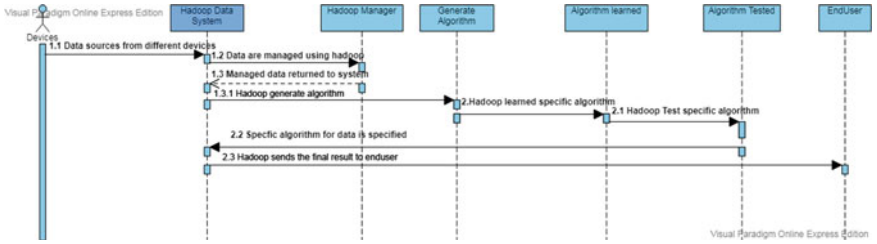

Fig. 2 Sequence diagram for our proposed algorithm

Step 10: Once, the above steps are done hadoop data system will switch over to end user tools.

3.2 Sequence Diagram

Initially data are accumulated from multiple sources. Data are being processed by hadoop data system and managed by hadoop data manager and outputted managed data are swapped back to hadoop data system. The hadoop data system will generate machine learning algorithm. According to the kind of data it will choose specific model and the outputted model will reversed back to hadoop data system. After completion of above steps hadoop will swap back to end user tools. In this section, Fig. 2 is expressing that the data sources which are being assembled from various devices are processed and managed. It also analyzes various algorithm and choose appropriate algorithm to learned specific model to predict diabetes.

4 Analysis

In our work, we have built the need of predicting techniques to measures the diabetes unlike the traditional models which doesn't provide enough efficiency, accuracy and fastest delivery. This technique possesses several data from EHR, R&D and other sources like smart devices.

By using existing technologies, it is possible to capture and send to a centralized database for analysis. Also, unlike most of the other proposed works, we used to gathered data from various devices and processed the data in hadoop data system and then processed data are being managed by hadoop data management and additionally it also applied machine learning algorithm such as RF, LDA, CART and K-NN provoked by hadoop. The machine learning algorithm has main benefits over the most other techniques as it provides more accurate throughput to user and it gains the performance rate of the model.

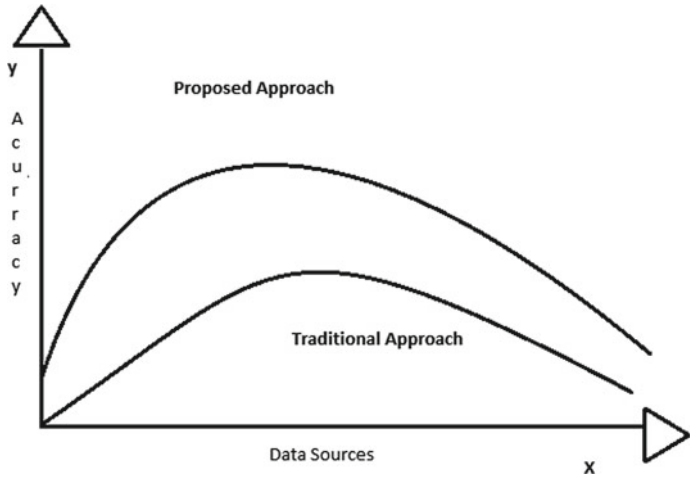

Fig. 3 Compares the traditional approach with the proposed approach shows accuracy will increase as data sources with increase

In our proposed work, considering all factors, we can say that the efficiency, accuracy and fastest delivery medical care at lower cost. This can be compared with the traditional approach by depicting them in the form of graphs for both the traditional approach and our proposed approach. It is depicted that data that we are getting from multiple sources are used to predict the diabetes. So, here accuracy perform a efficient role. Figure 3 compares the data sources with the accuracy as the data sources will increase accuracy throughput will also increase in proposed approach and decrease in traditional approach. Figure 4 is expressing the comparison of cost of traditional approach as compared to proposed approach the cost will decline in proposed approach.

5 Conclusion

Peoples are engaged in today's world in the feverish slots and not pickings any care of their own health, starring to difficulties of continuing disease such as diabetes. In this paper, a recent framework is suggested that utilize. This framework will analyze and predict diabetes Mellitus and providing way to improve healthcare complexity and delivering earliest potential working. As well as this framework is operate for self-treatment and also in future providing faster medical care within a chip costs. In this paper, it also provides many various machine learning algorithms such as RF, SVM, CART, LDA and K-NN to predicting data patterns. The frame work is working currently under development.

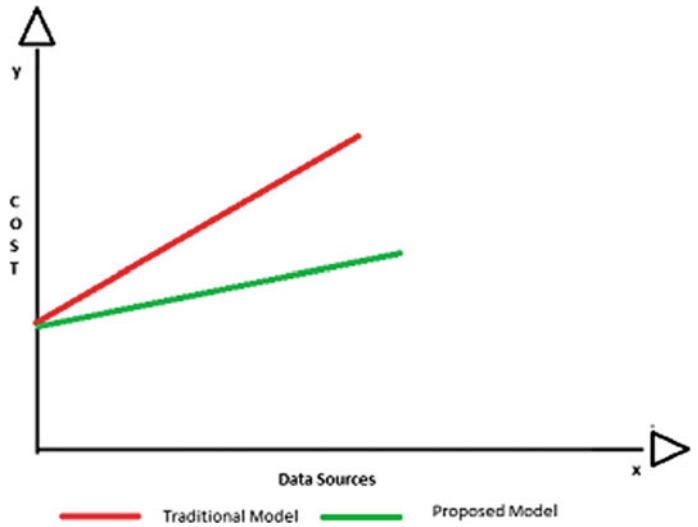

Fig. 4 Compares the traditional approach cost with the proposed approach and display the increase in cost in traditional approach and decrease in proposed approach

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Fourth Industrial Revolution: Progression, Scope and Preparedness in India—Intervention of MSMEs

Arindam Chakrabarty, Tenzing Norbu and Manmohan Mall

Abstract MSME (Micro, Small and Medium Enterprise) sector constitutes more than 99% of private firms operating in India which generate crores of jobs across the country. In fact, the MSME firms aim to support the large companies either in the form of outsourcing partners for supplying raw materials, W-I-P or adding value to one or few processes as ancillary to the big establishments. However, in the growing competition and the market complexity, the MSMEs have to compete with the large firms. The world is emerging toward Fourth Industrial Revolution (4IR) which not only prescribes for automation, speed, and prompt delivery mechanism but also it attempts to duplicate Human Intelligence in the form of Machine Learning or Artificial Intelligence (AI). In the dynamics of rapid changes across the Industrial Ecosystem, it is emergent for the MSMEs to re-module its business directions. The threshold level technology needs to be transferred, absorbed, and adopted by the MSME firms so that the can play a meaningful role in today's knowledge economies. This paper has explored the Scope and Preparedness for the sector and has prescribed desired Policy Reforms to make the transition smooth, value-adding and resourceful.

Keywords 4IR · MSMEs · Artificial intelligence · Threshold level technology · India

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1 Introduction

1.1 MSMEs in the World

The contribution of MSMEs across the globe has been found highly significant particularly as a change agent for rapid socio-economic development [1, 2]. Research indicates that the MSME sector has a positive association with the economic growth and developmental indicators equitably both in developing and developed nations of the world [3, 4]. The sector has been instrumental to absorb a large pool of manpower directly or indirectly worldwide.

1.2 Indian MSMEs: Status, Scope, and Achievements

Indian MSMEs have the capacity of absorbing around 40% of the total workforce that contributes almost 45% of manufacturing outputs worth of around 6% of manufacturing GDP and reserves the share of 40% of total exports of the country. It is observed that around 94% of the firms belonging to the MSME sector are not registered even though the growth of this sector has been recorded at around 11% per annum which is more than the average GDP of the country in recent years [5, 6]. However, with the implementation of Goods and Service Tax (GST) in India, the unregistered MSMEs are compelled to enroll as a part of legal bindings. The MSME firms have been largely facing a series of problems and inadequacy which are mostly in terms of lack of availability of resources and opportunities leading to high-end inefficiencies. However, India witnesses a minuscule of MSME firms that are performing at par with the big corporates while the larger section of Indian MSMEs acutely suffer from Industrial Sickness or pro-sickness. The financial package extended to such sick firms would not be able to address the root causes rather offering some other set of benefits which might result in a favorable outcome [7, 8]. Most importantly, the industrial development is a function of the ease, access, and successful use of technological development. The MSME sector essentially needs the constant support for skilling of its manpower and technology led transformational business practice. Barring a few Medium and high performing firms, it is difficult for Micro or Small firms to afford continuous investment for technological upgradation. It is indeed a great challenge for the policymakers and the promoters these firms to have a full-proof solution for its survival, growth and sustainability.

2 Review of Literature

MSMEs are deemed to be an accelerator of economic growth across the world [1, 2, 9]. There is a positive relationship between the growth of MSMEs and the growth of the economy in many developed and developing countries [3, 4, 10].

MSMEs are the backbone of the Indian economy as they play a pivotal role by making a substantial contribution to the economy. They contribute around 40% of gross industrial value, 45% of the export and are considered to be the second largest employment generator in the country [9, 11]. Therefore, MSMEs are a necessity for the nation as they ensure innovation, revenue generation, and employment generation, etc. [12]. MSMEs, notwithstanding, face several challenges in India such as lack of tangible resources [13], HRM related issues [14], issues related to power, raw material procurement [15], lack of adequate financial assistance from Banks, absence of sophisticated technologies, scarcity of resources, and lack of skilled manpower leading to ineffective marketing [16].

3 Objectives of the Study

The present study endeavors to:

i. Study and understand the progression of the Industrial Revolution with a special focus on the Fourth Industrial Revolution (4IR).
ii. Explore the scope and emergence of 4IR in India with special reference to MSME sector.

4 Research Methodology

The paper has been conceptualized responding to the call of the hour about the emergence of the 4IR in the world and specifically in the Indian subcontinent. The paper has attempted to understand how the 4IR has progressed over a period of time which has been presented with the use of relevant and reliable secondary information. Since the country has been growing as one of the fastest economies of the world and also aspiring to optimize its demographic dividend, it has become imperative to understand the scope and emergence of 4IR and how the Indian MSMEs can play a responsible role as it caters to almost the entire Indian industries barring a few hundreds of larger firms.

5 Analysis and Interpretation

Analysis I

The Industrial Revolution (IR) began with a view to meet the demands of growing population in terms of supply of products. The primary sector has its limitation and highly concentrated on agricultural produces, handlooms, and handicrafts products. With the landmark invention of Steam based Power and Low Productive Machines and other tools, the First IR took place in the mid of the eighteenth century which continued up to the first half of nineteenth Century. With the pace of technological development in consonance with the growing demand for higher productivity, the Second IR started from the second half of the nineteenth century to the mid of the twentieth century where the sector emphasized on assembly line and mass production techniques to cater to the need of the population. In the later part of twentieth century, the industry was dominated by growing advent of electronics, instrumentation, and computational devices, IT and automation, it introduced a new age of Industrial Revolution popularly known as Third IR. This period of IR focused on higher volume of production with superior quality, precision, and Quality Function Deployment (QFD). In fact, Total Quality Management (TQM) appears to be the prime focus among most of the learning and large firms. The emphasis of Product Development has been shifted to achieving excellence in Process Development since the outcome of the lead processes essentially improvise creating higher quality of product. We are now in the era of 4IR where not only the Production Operation Systems are being modified through continuous improvement process as prescribed by Deming's P-D-C-A Cycle but the sector intends to replicate Human Intelligence par excellence into the devised mechanism in practice. The flowchart of the progression of IR consistent with the timeline has been enveloped in Fig. 1.

Analysis II

The new regime of IR has been propelled by outstanding advancement of satellite and wireless technology and its successful adaption among the population like Mobile Telephony, access to Mobile led Internet, use of high configuration platform like androids, etc. The wave of such advancement was highly appreciated and absorbed by the Indians particularly the Youth population of the country.

The tremendous growth of mobile and internet services have revolutionized the economic growth trajectory of the world and, of course, this is going to impact the Indian economy in the coming decades. The vivid penetration of Smartphone tremendously enhances the use of Mobile Internet as compared to Fixed Line Portals. This has made a growing propensity and user friendly internet access platform for the Indian users that resulted in greater participation in mobile led e-commerce activities across the country. This has motivated the Indian users to prefer new business model [17]. Internet economy of India is projected to double from the existing (April, 2017) 125 billion USD to 250 billion USD by 2020 at the behest of phenomenal growth in e-commerce/m-commerce of which the value of transactions would reach around 100 billion USD through digital platform. The ambitious project of Digital India

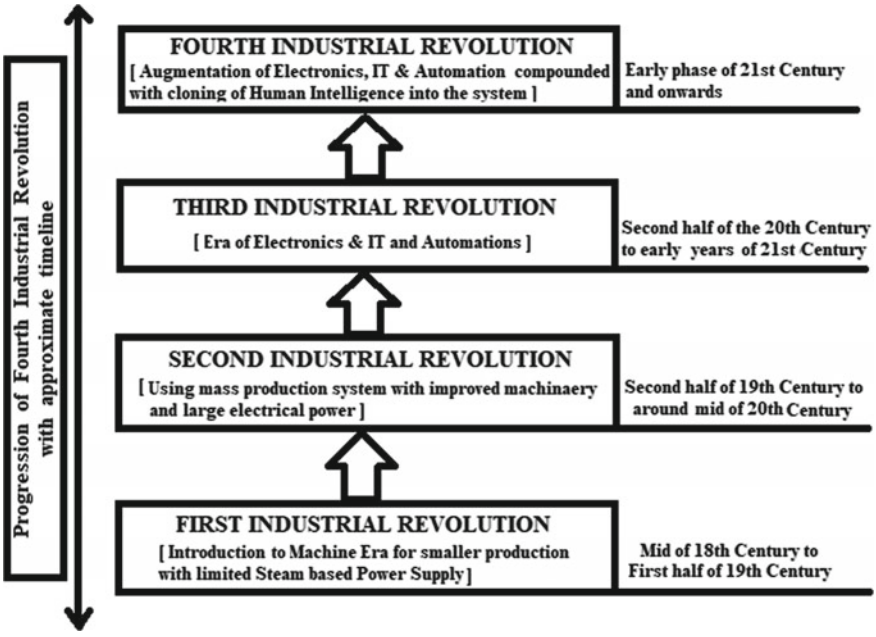

Fig. 1 Industrial revolution: journey ahead

Campaign intends to create online economy worth trillion USD by the year 2025 [18].

According to Worldometers—real-time world statistics, the present global population is around 7.6 billion of which it is estimated that almost half of the population are Internet users and surprisingly, around 50% of global internet users reside in Asia. Around 24% Internet users from Asia belong to India [19]. It is projected that the market potential for IoT devices in India would reach up to 9 billion USD by 2020 [20] as the country is poised to execute large scale IoT intervention projects to cater to its diversified reform policy [21]. All these above figures and observations signify that there is a growing market opportunity in creating, manufacturing and servicing IoT led devices in India which can be shouldered by the Indian MSMEs either as a support hub of large scale enterprises or the independent providers in the segment. This would depend based on the Competency Mapping of the MSMEs firms in terms of firm's core expertise, experiences, conformity of other value chain and the extent of absorbing and adopting new age technology within the least possible transition of time.

6 Recommendations

Based on the present study, it is imperative to understand the development of IoT led and other forms of digital ecosystem in the era of 4IR has been emerging as mammoth business opportunities where the MSMEs can play a leading role along with the larger firms. This transition needs certain policy reforms from the state as well as higher commitments by the enterprises operating in India since India is emerging as the fifth largest economy in the world and the second largest continent using part excellence technology. The sector can achieve enormous export opportunities in various countries of Asia, Africa and Latin America even a small segment of gulf nations since India enjoys a competitive edge over others in terms of its positioning as IT superpower, superior quality of human skill, competitive labor cost, and sustainable competitive advantage on the related domain trade. To achieve these agendas, the following recommendations may be incorporated:

1. The government should sponsor and organize massive skill development programs highlighting the necessary augmentations for creating devices related to IoT and other forms of digital and interactive ecosystem.
2. To reinforce the confidence among the smaller firms, the state may formulate time-bound financial incentives either in the form of tax exemption or extending case-specific subsidy so that financial aspect can be considerably supported.
3. The bank or Financial Institutions may be directed to promote firms for venturing into 4IR by allocating targeted budgetary provisions that should be disbursed in a time-bound manner.
4. The state must encourage Higher Educational Institutions like Universities, Colleges, and Research Institutes to take up innovative and need-based projects and applied research in the broader domain of IoT enabled devices so that the outcome of the research can move from lab to market. The present research has identified that people of India are keen to get IoT augmented high quality healthcare sector which can be prioritized along with other emerging areas.
5. Massive investment in the sector is essential in order to strengthen the infrastructure for delivering public utility services like health, education, Public Health Engineering (PHE), environmental protection etc., both in rural and urban areas of India in order to expedite rapid socio-economic transformation as prescribed by the United Nations' Sustainable Development Goals (SDGs).

7 Conclusion

The present paper is exploratory in nature which has been grounded by the latest dataset and information collated from most recent and reliable sources. The paper has attempted to showcase how 4IR has arrived and is knocking at the door. If we miss or delay to welcome, perhaps we would be compelled to invite ourselves to the

catastrophic consequence and would fail to get into the growth trajectory in the new millennium. India is about to encash its growing demographic dividends where it is inevitable to imbibe the youth with this new generation business model otherwise it would be detrimental to achieve the goals as doctrines by UN SDGs.

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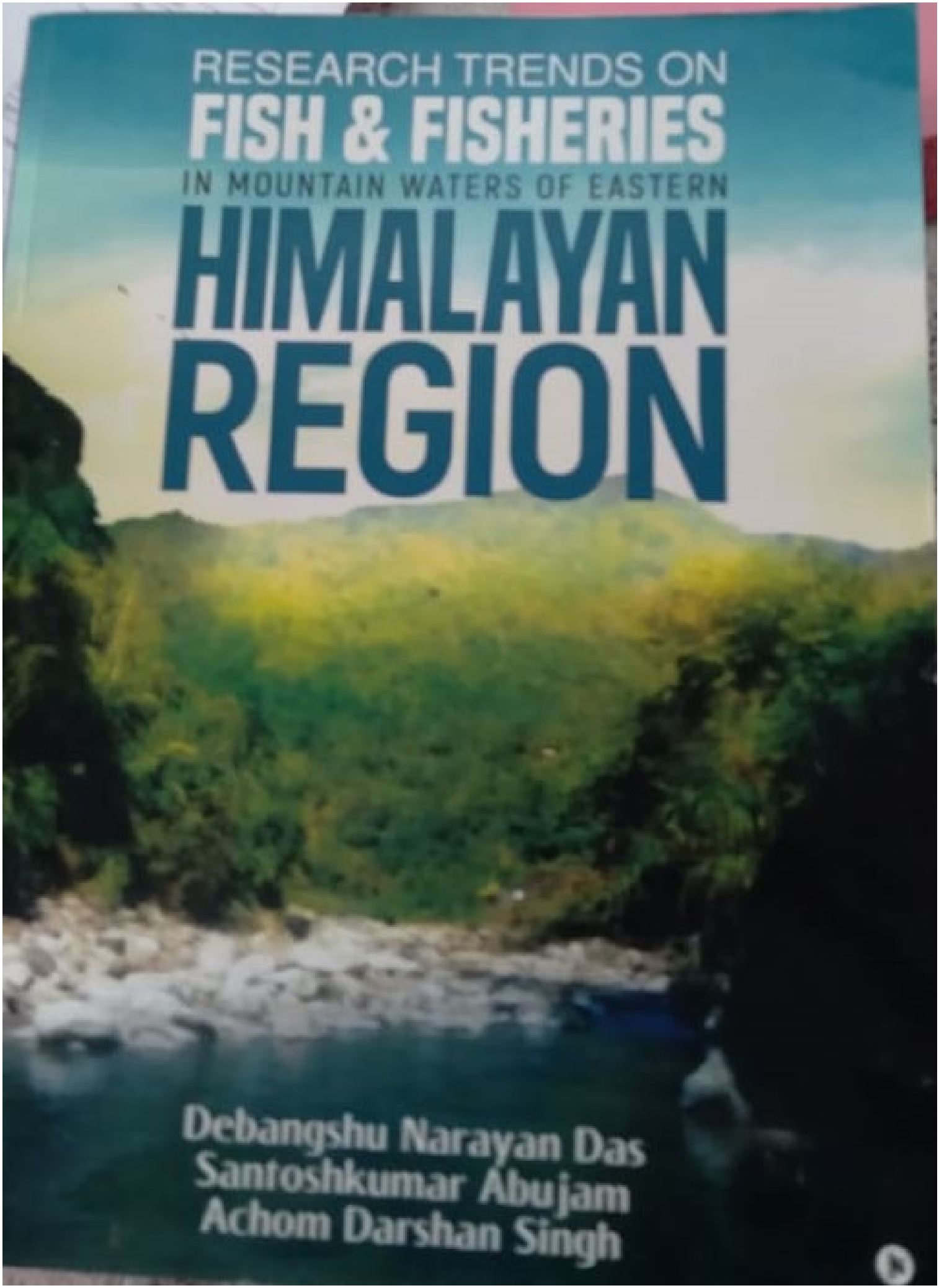
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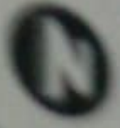

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Economic Valuation of Shalley Lake in Arunachal Pradesh

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Abstract

Natural lakes and wetlands provide goods and services to the human beings which are still underpriced. The values of lake are enormous in the present market context but due to non existence of price mechanism in the market for natural resources leading to its undervaluation. Without proper estimation of value, resources are bound to be underutilized. Further, due to absence of property rights and open access nature, its importance has never been realized in the market context. Economic valuation of the wetlands is necessary to understand the importance of wetlands in ecological functions and providing basic needs to us. Hence, alternative valuation by using surrogate market prices is needed to evaluate the stream of benefits received by the people. Therefore, in the present study an attempt is made to estimate the recreational and non use value of one of the surveyed lake i.e. Shalley Lake by using non-market valuation methods Contingent Valuation Method and Travel Cost Method.

Keywords: Wetlands, Contingent Valuation Method, Travel Cost Method

Introduction

According to Ramsar Convention Bureau, a wetland is defined as areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water, the depth of which at low-tide does not exceed six metres (Barbier *et al.*, 1997). The wetlands are lands transitional berween terrestrial and aquatic systems where the water table is usually at or near the surface or the land is covered by shallow water. For purposes of this classification wetlands must have one or more of the following three attributes: (1) at least periodically, the land supports predominantly hydrophytes; (2) the substrate is predominantly underdrained hydric

Smart and Sustainable Agriculture Through IoT Interventions: Improvisation, Innovation and Implementation—An Exploratory Study

Arindam Chakrabarty and Tagiya Mudang

Abstract From the dawn of civilization, the unending aspiration toward achieving excellence has been the paramount accelerator which is witnessed through different ages, i.e., Stone Age, Bronze Age, Iron Age, age of automation and information supremacy. The world is transforming into massive digital ecosystem. The comprehensive digital value system is being pioneered by developments in IT and ITES. Internet of things (IoT) is the culmination and assimilation of related instruments for sharing real-time data in a collaborative, harmonized and mutually exclusive manner to facilitate optimum decision-making process. In spite of technological advancement, the society survives on primary sector. So this is the high time to capitalize the threshold the technological knowledge into agriculture system so as to optimize resources, minimize losses and ensure achieving the spirit of sustainability. It is also interesting to see how the most advanced technology can be synergized in primitive farming techniques. The European and Latin American countries have been using IoT in agriculture in varied modes, dimensions and levels. These can be exemplified by glimpse of application like farming based on weather projection, real-life count of agriculture produces, real-life estimation for loss due to perishability or expiry, irrigation issues, controlling of infrastructure support for farming activities from distant location, census of cattle, etc. In fact, the concept of IoT is in still nascent stage in India. There are vast opportunities of IoT application in the country since India is primarily an agrarian society and around 60% population are engaged in this profession which contributes around 17% of share in GDP and feeding the elephantine population of the country. This paper would study various sparks of IoT system, its versatile application worldwide and possible intervention in India particularly in agricultural activities. The paper would explore innovative modeling for IoT integra-

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tion in agriculture system and its ease of implementation globally with emphasizing on Indian subcontinent.

Keywords IoT · Sustainability agriculture · Innovation · Technological advancement

1 Introduction

Concept of IoT

IoT which is popularly known as **Internet of things (IoT)** is the systematic arrangements of smart devices, equipment, objects, animals or people connected with each other assigned with UIDs (known as unique identifiers) and having the features to transfer data over a network.

Today, in every field, the Internet of things (IoT) is getting recognized and becomes significant for agriculturist, professionals, agencies, etc. to understand the phenomenon of its power to improve business and other activities.

IoT basically consists of four basic architectures.

i. **Power-Efficient system**—The inverse proportion of high performance with low battery consumption gives a significant edge during the design of electronic system.
ii. **Cloud computing**—IoT generates a huge mass of data, and these data collected from the device need to be stored and processed in the server. To process such volume of data, there was an inception of cloud computing to anticipate the need. Cloud computing refers to the provision of different services through the Internet. This phenomenon includes tools and applications in the form of data storage, servers, databases, networking and software.
iii. **Big data**—IoT works on devices like radio-frequency identification (RFID) sensors, smart network mostly real time. These devices are spread across every field to capture a massive flux of big data.
iv. **Network connectivity**: Internet connectivity is like oxygen for IoT without which the device cannot work. In order to communicate, the Internet connectivity is essential where each device, object, etc., is represented by an IP address. The smart devices are connected via Internet in a way that it captures and optimizes every bit of data obtained in everyday life.

Dynamics of IoT

The territory of IoT is limitless and is heading beyond computers, laptops and smart gadgets. Nowadays, it is moving toward linked cars, smart homes, connected wearables, smart cities and smart health care. In the nutshell, it is a connected life. As per Gartner report, it is predicted that by year 2020 the number of connected devices across all technology in the world shall reach 20.6 billion.

Year	No. of connected devices
1990	0.3 Million
1999	90.0 Million
2010	5000 Million
2013	9000 Million
2025	1000 Billion

Source https://www8.hp.com

The above table gives the estimation about the number of devices which get connected in the near future. The study conducted by Hewlett-Packard which shows that these devices will fill the space between physical world and the digital to enhance the value, productivity and quality of life, society and industries.

Dynamics of Agriculture:

S. No.	Various domains of agriculture	Description
1	Agronomy	It is the branch of agriculture which deals with the study of crops and soils for the purpose of production of various crops like food crops, fiber crops, sugar, oilseeds, etc., for the purpose of better food production and to control the diseases
2	Horticulture	This branch of agriculture mainly deals with the productions of fruits, vegetables, flowers, ornamental plants, spices, condiments, beverages, etc.
3	Forestry	The forestry branch deals with production of large-scale cultivation of perennial trees for the purpose of wood, timber, rubber, raw materials for industries, etc.
4	Animal husbandry	This branch of agriculture deals with the practice of raring, breeding and raising livestock in order to provide food for humans and to provide power (draught) and manure for crops
5	Fishery science	The science that deals with practice of breeding and rearing fishes. This may include various marine and non-marine fishes, shrimps, prawns, etc., for the purpose of food, feed and manure
6	Agricultural engineering	This branch of agriculture is a branch of engineering also which deals with farm machinery for preparation of field, cultivation, pre- as well as post-harvest process like soil and water conservation engineering and bio-energy

(continued)

(continued)

S. No.	Various domains of agriculture	Description
7	Home science	Home science branch deals with application and utilization of agricultural produces in an optimize manner so as to provide nutritional security, including value addition and food preparation

2 Sustainable Farming

Sustainability is the most prolific buzzword in the present time. The traditional concept of business narrowly focuses on product, productivity and profit. With little or no concern toward environment, natural resources and ecology. The reason behind this ideology was driven by either the availability of abundance of resources or least awareness about nature or natural resources. As the human races are moving through knowledge age, it has been visualized through series of research outcomes, experimentations, etc., that the earth is passing through at alarming stage. The greed of comfort and increased ease of convenience have mesmerized the world population toward innovative products where the virgin resources of nature have been ruthlessly exploited of which hardly miniscule of them can be reversible back to nature, partly of them can be recyclable, and majority of the material have become wastes that cause pollution and diminish ecological balance. On the other hand, as human societies are growing by numbers, and especially in some Asian countries, the growth rate exceeds the G.P rate. As a result of that, the human endeavors have started to understand the resource scarcity for a long-term perspective. All these limiting constraints have necessitated the emerging concept of sustainability. According to Brundtland Commission Report 1987, sustainability can be defined as: "Sustainable development is the development that meets the needs of the present without compromising the ability of future generations to meet their own needs." Agriculture has changed dramatically, especially since the end of World War II. Food and fiber productivity soared due to new technologies, mechanization, increased chemical use, specialization and government policies that favored maximizing production. Today, sustainable farming becomes vital for the health and welfare of our planet. While modern industrial agriculture is highly productive and can produce a massive amount of plants within a harvest season, it also introduces many damaging and long-term problems that can only be solved through sustainable practices. With the decline of the farming environment around the world today, here are five reasons why sustainable farming is a rational solution to our agricultural needs. Sustainable farming system integrates three main goals—environmental health, economic profitability and social and economic equity. A variety of philosophies, policies and practices have contributed to these goals. People in many different capacities, from farmers to consumers, have shared this vision and contributed to it. Technologies and production approaches that meet ecological environmental development requirements

are being used for sustainable agriculture. Sustainable agriculture requires the prevention of ecological crises like major accidents, with strong negative impact on the environment.

IoT intervention in Agriculture

The inception of IoT technology has been a boon in the agriculture domain. The use of IoT enables smart farming which helps in reducing the wastage and increasing productivity through efficient production and operations of agriculture raw materials. The use of IT and devices like robotics, automated hardware, sensors and control system in IoT makes possible for precision farming and becomes popular among the agriculture organizations across the globe. To monitor the fields and agriculture activities, the agriculture drone became helpful gadgets for the farmers. This agriculture drone is easy to use, helps in saving time and monitoring crop health and integrates geographic information system (GIS) mapping.

IoT has played an important role in managing the supply chain of agriculture activities. The RFID and cloud computing technology integrate the data and information of production, distribution and safety of quality in the agricultural supply chain effectively which combine the farmers with the IoT and make transparency of the entire agricultural supply chain process. This helps in monitoring and tracing the quality of agricultural materials. Information of every aspect including the production, procurement, storage, transportation and sale on agriculture supply chain management will be processed by IoT. The system sends the exact requirements in terms of quality and quantity of agricultural products such as pesticides, fertilizers and seeds to appropriate places for meeting the needs of farmers in right price at the right time. As much as environment issues are concerned, IoT-based farming benefits in terms of effective usage of water and treatment. As a result, all of these factors will eventually lead to higher revenue generation. The intervention of IoT in agriculture can be advantageously applied in the sphere of agriculture.

3 Review of Literature

Kidd (2012) stated that the application of Internet of things shall provide the base for future sustainable rate of agriculture to meet the estimated growth in the demand for food, with respect to natural constraints, which delivers system-level benefits in terms of biodiversity at different levels (field, farm and landscape). These system will facilitate the land use management and helps in making decisions in the area of production whether to increase or to decrease based on the data gathered. Such a system will give a basis to support farmers in managing their agronomy practices to satisfy local biodiversity requirements and natural resource limitations. Duan (2012) concluded that IoT cannot only improve the quality of agricultural product, the efficiency of agricultural production and the level of agricultural product supply, but also efficiently solve the emergent dispatch of food in special situation. Kanget et al. (2012) states that IoT system helps recognize the information of things such as environmental changes or crop growth changes through the monitoring of environmental

information based on the sensors connected through the Internet. Such information is expected to provide the methods to identify the surrounding environments of things through the sensing, delivery and exchanges between differentiated devices. In addition, this information is likely to enable the search and grouping of physically separated growth environments according to various conditions and their management under various conditions corresponding to environmental or other pertinent changes. Moreover, various sensors connected through the Internet are expected to maximize the quality and efficiency of management by conveying the information on the occurrence of abnormal growth to users or controlling irrigation systems through the transmission of control demands. Patil and Kale [5], in their study, proposed an approach with Internet and wireless communications—remote monitoring system (RMS). According to them, this system received real-time information which allows the farmers to cope up with and even benefit from these changes. Due to highly localized nature of agriculture information specifically distinct conditions, it is very challenging task that needs to provide such insights. The complete updated and historical environmental information is expected to help to achieve efficient management and utilization of resources. Zulkifli and Noor [11] observed that with the introduction of RFID technology and wireless moisture sensor network (WMSN) in the agricultural and farming sector, growing crops and plants can be greatly optimized. WMSN reduces the wiring and piping costs and facilitates installation and maintenance in large areas. Apart from decreasing labor costs and water requirement, the application of smart technology in agriculture is very crucial in terms of production. Hence, the WMSN system apparently accomplishes the most technology to enhance the present irrigation systems. The moisture sensors for the soil are continuously improving and becoming reasonable and suitable for massive deployment in the WMSN applications.

4 Objectives of the Study

i. To explore the nations that are practicing any form of smart farming system by reviewing recent and relevant literatures.
ii. To study the scope and opportunities of IoT interventions in Indian farming system.

5 Research Methodology

The paper is exploratory in nature. The purpose of this paper is to understand and study how Internet of things (IoT) has been used for excelling agricultural practices across the globe. The research study has been carried out using reliable secondary information from referred articles, research outcomes, policy papers, etc. The paper also attempted to showcase how the IoT ecosystem can be incorporated in India farming practices. For developing the conceptual framework, inputs from ground level practitioner have been taken for developing such models.

6 Analysis and Interpretation

Analysis-I
IoT intervention in sustainable farming across the world:

Internet of things (IoT) is the assortment of new age instrument that has initiated Fourth Industrial Revolution. The application of IoT has been emerging in the varied fields of agriculture. The developed nations have been experimenting how best the IoT devices and blockchain technology could be assimilated to improve effectiveness and efficiency of the existing modern farming practices. Various research papers have focused on the multifaceted experiences of different countries through their intensive research work. The following table reflects the set of countries who have been using the smart agricultural practices across the world which have been endorsed by relevant research study.

Smart agricultural practices by different countries

S. No.	Name of the country	Source
1	Israel	Lawhon and Schwartz (2006)
2	Brazil	Maia et al. [2] Pivoto et al. [6]
3	Canada	Steele [8] Stanford et al. [7]
4	China	Chunsheng and Ning (2010) Chen et al. (2014) TongKe [9]
5	South Africa	Evans (2018) Masinde [3]
6	Netherlands	Long et al. [1] Van Gossum et al. [10]
7	Australia	Nukala et al. [4]

Analysis-II
Scope of IoT in Indian farming system.

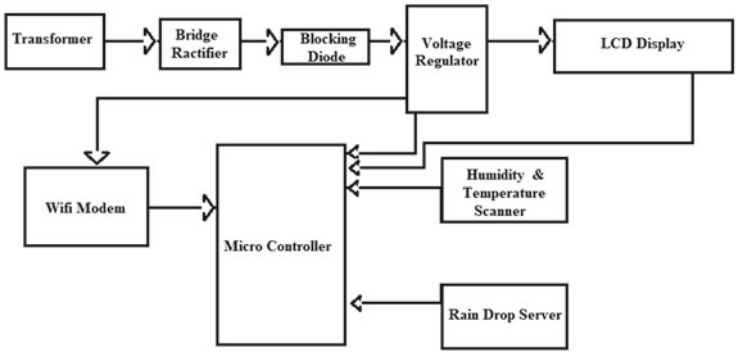
(i) Irrigation system.

The model of smart irrigation provides the solution for the issues of the irrigation system in the conventional farming system and maintains the optimum conditions for their crops. Crops need sufficient water and ideal temperature to grow in the environment. This will help in improving the quality of the plant and productivity of the field too. With the application of IoT devices like smart phones and remote computers, the worker can access the cloud storage to retrieve the data obtained by the sensor devices. The farmer can control the water supply system with the help of the smart devices and can supply the water requirement directly to the root of the

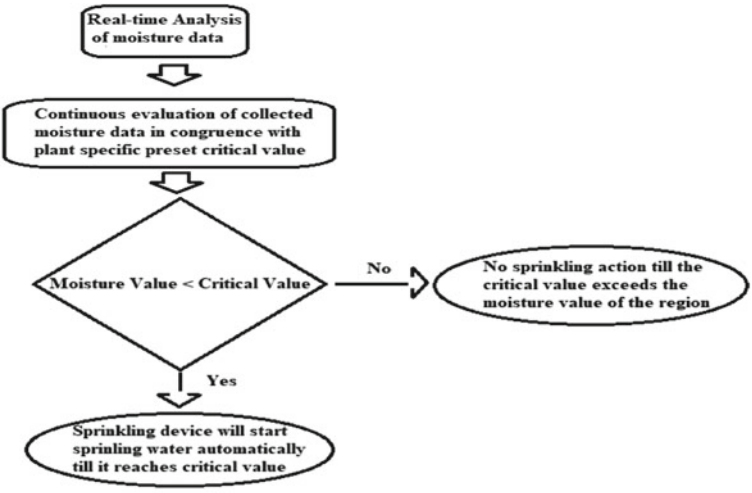
plant. This mechanism will help in weed control in the field since the water supply will be limited to the plant only.

(ii) Weather-adjusted agriculture system.

IOT weather reporting system has application in agriculture as well. Weather reporting system based on Internet of things (IoT) application has the ability to foresee and measure about all climatic conditions such as temperature difference, level of humidity and rain. IoT-enabled weather reporting system has been designed with the accessories like LCD display, Wi-fi modem, transformer, bridge, microcontroller, voltage regulator, microprocessor, sensors, etc.



Block Diagram for IoT enabled Weather Reporting System for Farming Excellence



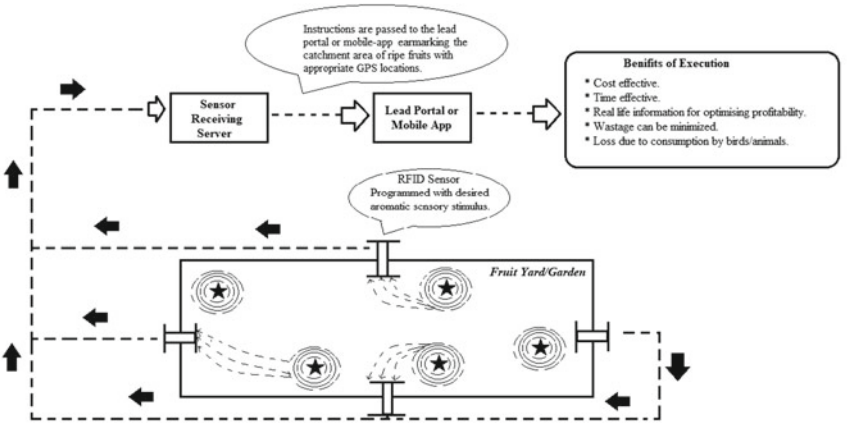
Flowchart of IoT guided smart sprinkling system in Agriculture
Development by Arindam Chakrabarty & Mudang Tagiya

(iii) IoT-controlled sprinkler mechanism.

Smart sprinklers can simplify the garden and agriculture and help in reducing the water consumption. The smart system works on data from the sensors, weather forecasts and crop-care database to ensure the water requirements and provide enough moisture in the right time.
Algorithm for this mechanism.

Step 1: The dedicated moisture sensor shall be designed to detect the moisture in the environment.
Step 2: The smart sensor is installed in the agriculture field accordingly.
Step 3: If the moisture level in the air is less than the critical limit, immediately a message will be sent to the sprinkling system; else, no action will be initiated.
Step 4: The sprinkling system will sprinkle the water immediately as per the instruction.
Step 5: The turning on and off of the sprinkler shall be done based on meeting the moisture value accordingly.

(iv) Estimation and Quality of fruits, pest control, weed control, etc., Using Image Technology.

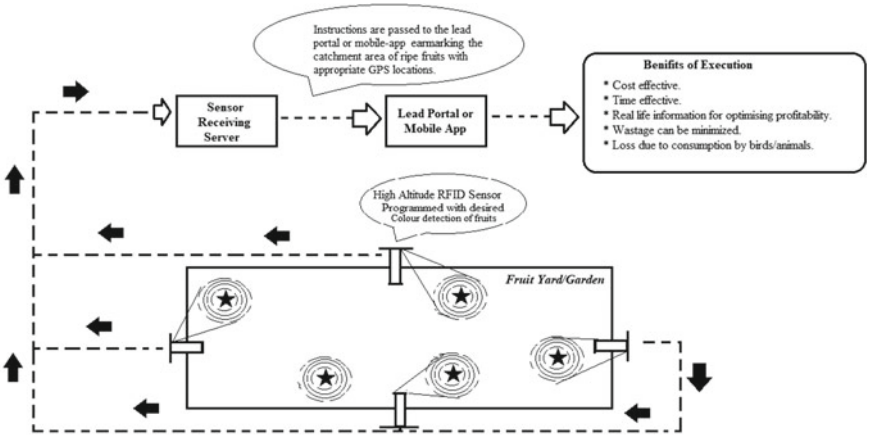


IoT Based Efficient and Sustainable Fruit Plucking Mechanism baseed on RFID sensor using aroma as Stimulus

Algorithm of this mechanism:

Step 1: Dedicated RFID sensor shall be designed which can detect the specific aroma of ripe fruits, and it could transfer to server.
Step 2: RFID sensors are installed in the fruit yard/garden to detect the aroma of the ripe fruits.
Step 3: The high concentration of aromatic stimulus produced by the ripe fruits will be captured by the installed RFID sensors and converted into suitable information about the nature and positioning of the fruits in the large area fruit yard/garden.

Step 4: The captured information is then sent it to the server.
Step 5: The appropriate instructions shall pass to the lead portals or mobile app earmarking the catchment area of ripe fruits with appropriate GPS locations.
Step 6: The farmers may execute the actions and receive the benefits accordingly based on the data retrieved from the system.



IoT Based Efficient and Sustainable Fruit Plucking Mechanism baseed on RFID sensor using Colour /Pigment as Stimulus

Algorithm of this mechanism:

Step 1: Dedicated RFID sensor shall be designed which can detect the specific color or pigment of ripe fruits, and it could be transferred to server.
Step 2: RFID sensors are installed in the high altitude in the fruit yard/garden to detect the color or pigment of the ripe fruits.
Step 3: The variation or change in the color of the ripe fruits will be captured by the installed RFID sensors and converted into suitable information about the nature and positioning of the fruit in the large area fruit yard/garden.
Step 4: The captured information is then sent it to the server.
Step 5: The appropriate instructions shall be passed to the lead portals or mobile app earmarking the IoT system attached with sensors, and other devices in the field processed the collected data to inform quick action. Remotely monitor for specific pests to understand their activity, location and patterns. This can be done by linking trap stores pond and inform level of specific pest activity followed by monitoring and collecting data to take accurate and quicker anticipation.

Here are four ways, the IoT is revolutionizing pest control in the food industry.

- Prediction and preparation against infestations
- Alerting about the signs of infestation
- It discourages the uses of chemicals
- Handling current issues.

Image analysis to distinguish between the crop and the weed species

i. Fishing—Quality of water is determined by the contents of pH, presence of metals, dissolve oxygen and foreign objects, etc. The most important factor in the production of the fish is the availability of quality water.
   The IoT system consists of pond regulator which uses sensory device to check the quality of water in the pond. The sensor captures the activities in the pond and further transfers it to the cloud location for storage. The integrated system is designed in such a way that it will have the capacity for remote operation through sophisticated designed mobile application assessing the data collected by the sensors and also controls the activities of the pond regulator. The regulator will manage the smart feeding system for the fish and the water monitor system for the pond which will help the owner of the pond in managing more than one fish pond from single mobile device. This mechanism will help in reducing the costs of management of fishing breeding activities.
ii. Tracking of domesticated animals–Hilly and tribal areas.
   RFID application in animal tracking enables tagging of domestic animals by various countries which helps them in tracking their animals. The tracking is done using radio-frequency identification (RFID) chip which is associated with the tag. This tag is attached to animals (domesticated.) by clamping on their body parts like ear, horn rim, planted inside the animal. Insertion can be done in various places depending on animal (Floyd 2015).

7 Conclusion

The contribution of agriculture in the GDPs of the developed nations has been decreasing in comparison with the service sector and manufacturing. This is simply because of the rapid industrialization, infrastructure development, urbanization and growth of populations. All these factors have been encroaching and shrinking the cultivable lands. On the contrary, the decreasing fertility with alarmingly increasing toxicity in the soil and environment, climate change has adversely impacted on agriculture produce. Within the limiting constraints, the sector needs to be vibrant, value-added and efficient so that the future of human civilization can be sustainable. This paper has attempted to showcase that the assimilation of high-end IT ecosystem with the farming system would be a sustainable solution for the future. The advancement of information technology has been emerging through a series of transformations. Now, it is the age of Internet of things (IoT) and blockchain technology. As per CISCO report, 500,000 million devices are likely to get Internet connected by 2030. The smart devices like sensors, camera, etc., generate data through which IoT examines, combines and delivers insights for decision making. The IoT will be the hub of devices that gathers data in the environment and communicate over the network. As per the recent study, it is calculated that 50% of all US food produce is thrown away. This study essentially has explored various existing and emerging applications

of IoT in agriculture sector particularly that suits the nature and aspiration of Indian farming system.

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Editor

Muthu Mathirajan

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Preface

The role of Business Analytics and Intelligence (BAI) in solving descriptive, predictive and prescriptive business problems, considering Big Data, has increased manifold in recent years, due to increasing power of Information and Communication Technology. Particularly, many companies are utilizing the BAI as competitive weapon. Understanding the importance of BAI in today's business environment, both Analytical Society of India (ASI), functioning from IIM Bangalore since its inception and Operational Research Society of India Bangalore Chapter (ORSI-BC), functioning from IISc Bangalore since its inception are being jointly organizing an International Annual event on BAI since 2013 onwards to create a platform and facilitate knowledge sharing on advanced data analytics, business analytics, Big data and business intelligence for distinguished academicians, practitioners, and researchers from academia and industry from all over the world. Accordingly, the 6th International Conference on Business Analytics and Intelligence, scheduled during 20-22 December 2018 (ICBAI-2018), accepted 175 presenters' (comprising about 45 percent from Industry and about 55 percent from Academic from all over the world) full-papers, out of 450+ extended-abstracts' blind review processes, discussing related to descriptive, predictive, and prescriptive analytics in all functional areas of management and engineering, are presented in the e-proceeding.

On behalf of the organizing committee of ICBAI-2018, I take this opportunity to express our sincere thanks to those who have helped directly or indirectly to bring out this e-proceeding. I acknowledge the support of every executive committee members of ORSI-BC and ASI for their sustained support in organizing the ICBAI-2018 and coming out with e-proceeding. I am thankful to the sponsors: State Street Global Advisors, Indian Institute of Science, Sabre Airlines Solutions, EY Bangalore, Reva University Bangalore, and Canara Bank IISc Branch Bangalore of ICBAI-2018 for financial support towards the ICBAI-2018 and publishing of this e-proceeding.

The e-proceeding would not have been possible without the support of the contributing authors, so I am thankful to them. Mr. Agnel Fernando and Ms. Anita, Secretarial Assistant for ICBAI-2018 and Research Scholars: Mr. Vigneswaran, Mr. Akhil Joseph, Mr. Balasubramaniam, and Dr. M. Vimalarani, who have worked with dedication and have spared significant amount of their time to bring successfully both ICBAI-2018 event and its e-proceeding. I am gratefully acknowledging their support as well. The publishers have extended their full cooperation to bring out this e-publication on time. I record my appreciation to them.

Editor

Dr. M. Mathirajan

Editor

Dr. M. Mathirajan has been working at the Department of Management Studies, Indian Institute of Science (IISc), Bangalore since April 1986 with various academic/faculty-positions. Currently he is a Chief Research Scientist at IISc, Bangalore. He received M.S. (Engineering) degree by research in Applied Operations Research area, and PhD degree in Operations Management area from the Faculty of Engineering, IISc, Bangalore. In addition he holds a M.Sc degree in Mathematics of Madurai Kamaraj University, and Post Graduate Diploma in Operations Research (OR) of Anna University, Chennai.

During May 2008-May 2010, Dr Mathirajan was with Anna University of Technology, Tiruchirappalli, on deputation, and he was the Professor of Planning and Development at the University level and he was also the Professor and Head of the Department of Management Studies of the Anna University of Technology, Tiruchirappalli.

Dr Mathirajan was a post-doctoral fellow at Singapore MIT Alliance (SMA) of Nanyang Technological University, Singapore. He was also a visiting consultant at Sultan Qaboos University (SQU), OMAN. Dr Mathirajan was selected and nominated as young Indian-representative of Operational Research Society of India (ORSI) to present a paper in the 1999 Fall Annual Conference of ORSJ, TOKYO, JAPAN.

Dr Mathirajan's PhD thesis was adjudged as best thesis for "M. N. Gopalan Award of 2002-Annual Convention of ORSI". Dr Mathirajan's research interests are in the development of mathematical modelling and heuristic methods for the problems related to Industrial Engineering, Operations, Logistics and Supply Chain Management in Manufacturing, Service and Container Terminal Management areas. He has published over 175 research articles. He is a co-author of three books [published by Person, PHI and Allied Publishers respectively].

He has guided a number of graduate and post-graduate projects. So far nine dissertations were awarded PhD degree under his guidance in IISc, Bangalore. Currently he has been guiding 5 doctoral research students at IISc; and he has examined several PhD theses from various higher learning Institutes (such as IITs, IIM, NITs) and Universities (such as Anna University Chennai, Central University Pondicherry, Gandhigram Rural University, Madurai Kamaraj University, Bharathiar University, Delhi University, Dr. MGR University).

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Awareness and Affinity towards Green Products among Young Generation: A Case of Arunachal Pradesh

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Abstract— **Environment has become a major issue for the sustenance and survival of living creature. Human societies aspire for continuous development i.e. development of technology, creation of innovative product, enhancing conform and greater communication. These compel to go for mass exploitation of resources that essentially include natural resources. Many a times the human beings overused and particularly most of them are irreversible in nature. In-fact it is an alarming situation, that highest effort should be given to reduce man-made pollution and environment degradation. The concept of green product has been evolved with the principle and commitment of the human races to use or exploit natural resources as least as possible i.e. required for smooth functioning of the civilization. This would enhance the scope for future generation for their survival, growth with sustainability. This mission can only be achieved if the new generation has environmental awareness and affinity towards using green products. The awareness generates through literature studied during school days, the value proposition and commitments of the family and the practices of social groups concerning the issues of the environment. On the contrary it is also imperative to understand whether the society has been adopting green products, whether the green products are available, accessible and affordable by the consumer in the market they operate. This study essentially would attempt to establish relationship among different variables which could be important for enhancing higher use of green products. The study area has been chosen from the largest state of north-east which is coveted by flora and fauna and largely dominated by forest area. Since the study is on understanding the level and intensity of purchase behavior intention of target population, adequate representative sample belonging to young age group of the state has been captured for collecting adequate information to fulfill the research objectives. As the paper is empirical in nature, the data set has been tabulated an analysis using SPSS, AMOS package. The study shows that 'Attitude towards environment' and 'Attitude towards Green Products' of the respondent – consumer towards 'Purchase Intention' for green products. The model is over justified and fit as the R^2 value is 0.87 i.e. 87% of the data set satisfied the model.**

Keywords **- Green product, Sustainability, Affinity, Young Generation, Arunachal Pradesh**

I. INTRODUCTION

Green products are energy efficient, durable and often have low maintenance requirements, free of ozone depleting chemicals, toxics compounds and don't produce toxic by-products. Often made of recycled materials or content or from renewable and sustainable sources.

Green product is defined as:

Green products are typically durable, non-toxic, made of recycled materials, or minimally packaged. Of course, there are no

completely green products, for they all use up energy and resources and create by-products and emissions during their manufacture, transport to warehouses and stores, usage, and eventual disposal. So green is relative, describing products with less impact on the environment than their alternatives.

(Ottman -1998, p. 89)

Green product is one of the most popular buzz words in the field of business and academia. In fact the growing concern of environmental issues has compelled both the seller and buyer towards adopting green movement as per as products and services are concerned. The WTO declaration of sustainability reveals that people of today should utilize environmental resources in such a fashion that the upcoming generation would also be able to equitably exploit such resources. The entire world is principally agreed committed to emphasis on usage of renewable products so that the depletion in the environmental resources could be minimized up to a certain extent. Researches are going on how to compensate or replenish the losses or exploitation of resources in order to balance physical, chemical, biological equilibrium of the universe. This should not be a statue of policy rather the policy should be visible flowing in the system through regular implementation and interventions. Otherwise the entire world would succumb the most detrimental ever policy paralysis. This paper would attempt to investigate how the policy framework on sustainability and green issues are being penetrated in the peripheral part of India. This research work would essentially manifest what extent the people at remote corner of India are aware, eager and actively participate in green movement in the same rhythm and spirit as the entire nation in convergent with global expectations and practices.

Literature Review:

Behavioral intentions are defined as a measure of a person's relative strength of purpose to execute certain behavior, **Ng, S., & Paladino, A.** (2009). According to **Rashid, N. R. N. A. (2009),** the green purchase intention as the probability and willingness of an individual to give preference to green product over conventional products in their purchase considerations. However referred green purchase intention as a determination to act in a certain way, **Ramayah et. al (2010).**

Rezai, G., Mohamed, Z., & Shamsudin, M. N. (2011, June) in their study, it was found that there is a significant differences among the respondents' awareness towards green food and age, geographical area, education level and income. The study also indicated that green food is not only about being organic but it also encompasses the concept of food safety, health issues, environmental hazard as well as animal welfare. Thus, the study shows that the target group was aware of the green concept which is a strong indicator of consumers' intention to go green in food consumption.

A conceptualized model developed by **Chan, R. Y., & Lau, L. B.** (2000) consisted of environmental concern, environmental knowledge, green purchase intention, actual purchase behavior and man nature orientation. In the study it was suggests that actual purchase behavior was highly dependent on a person's green purchase intention and the model was aligned with Theory of Reasoned Action and Theory of Planned Behavior by **Ajzen, I.** (1991). The dependent variable – green purchase intention in **Chan and Lau** (2000) study has been measure by using as a single dimension with four statements.

Chen, Y. S., & Chang, C. H. (2012) Green perceived value would positively affect green trust and green purchase intentions, while green perceived risk would negatively influence both of them. Furthermore, their study demonstrates that the relationships between green purchase intentions and their two antecedents – green perceived value and green perceived risk – are partially mediated by green trust. Hence, investing resources to increase green perceived value and to decrease green perceived risk is helpful to enhance green trust and green purchase intentions.

However, the definition given by **Han et. al** (2009) on green purchase intention as 'the likelihood of the hotel consumers of visiting a green hotel, engage in a positive word-of-mouth behavior, and willingness to pay more for the green hotel'. The conceptual model developed in their study aims at investigate the relationship between attitude toward green behaviors, overall image and green behavioral attention among general hotel consumers who were age range 18 years old and above. The study was conducted in U.S. The result reveals that there were three dimensions which are involved viz. visit intention, word-of-mouth intention, and willingness to pay more.

Another study conducted by **Qader and Zainuddin** (2011) aims to identify the

influence of media exposure on purchase intention of lead-free electronic products (green electronics) amongst 170 lecturers in Universiti Sains Malaysia.

They abstracted the green purchase intention as an individual‟s plan to involve in some action within a specific time and the probability that individual will perform an eco-behavior. **Qader and Zainuddin** (2011) have operationalized their dependent variable – green purchase intention as a single (1) dimension with three statements to measure intention.

Joshi, Y., & Rahman, Z. (2015) In their study draw the conclusion that the consumers are willing to buy green products although this will somehow does not translate into actual purchases. The authors viewed that companies offering green products should not view their offering just as a unique product that presents new business opportunities, and overprice the product on the basis of it being 'green'. This 'green thinking' should be a part of an organization's work culture and ethics. The company should want to make products that are safe for the environment and accessible to everyone. The retailer should keep a variety of products so that consumers have better and broader choice ranges, thus really encouraging consumers and society to 'go green'.

For the purpose of this study, green purchase intention was abstracted as a one-dimension based on **Chan and Lau** (2000) and **Qader and Zainuddin** (2011) definitions. In addition, the definition of this dependent variable will be consistent with **Rashid, N. R. N. A.** (2009) which defined green purchase intention as the probability and willingness of an individual to give preference to green product over conventional products in their purchase considerations.

Objectives of the study:

1. To study and exhibit the domain of green products in Indian context.
2. To explore the level of awareness and affinity of green products among young generation in the state of Arunachal Pradesh.
3. To understand the influencing factors that enhances purchasing of green products in the study region.
4. To formulate and establish a research frame work incorporating all the influencing variables with reference to purchasing intention of green products.

Purpose of Research:

The purpose of the research work is to understand the level of awareness about

green products and purchasing intention among young generation in peripheral state of India. The objective of the study has been rounding on the core ideas i.e. the extent of attitude of the respondent towards environment and corresponding attitude towards green product which may possibly interact and influence on purchase intention for green products.

Research Methodology:

The study is conducted based on empirical analysis of data set which has been collected from target sample. The study was primarily focused on young generation of the state under study. To capture the views and observation of young generation the sampling framework was designed taking students of different level as stratum. For this purpose the final year students considered representing higher secondary level, undergraduate and post-graduate level. Two stage stratified random sampling method was adopted in order to minimize data inconsistency and biases. Details of sampling plan and data sources are illustrated below:

Sampling Frame:

Two stage stratified random shall be adopted to select the respondent. The unit of sample would be student – respondents who would be appearing final year/semester in academic year 2018 – 19 in respective institution.

Table I

Stage 1 – Randomly selected educational institutes (Govern and Private)					
Study Region	Name of Stratum (First Stage)	Total no. of Institutions in the study region (Govt. & Private)		No. of Institution selected (First Stage)	Types of Sampling
State Capital of Arunachal Pradesh, India	High Secondary Schools	Govt.	8	2	First Stage stratified Random Sampling
		Private	10	2	
	Colleges	Govt.	03	1	
		Private	08	2	
	Universities/Institution of Higher learning	Govt.	03	1	
		Private	02	1	

Source: *http://www.apdhte.nic.in/colleges.htm, **http://www.rgu.ac.in/, DDSE capital complex, Arunachal Pradesh

Design of research instrument:

The research instrument was designed to understand the influencing factors which impacts on purchase intention for green products. Based on review of leading research papers and interaction with the domain experts and also results of pilot study, a proposed model was designed using assumed independent and dependent variables. All the variables were measure using 5-point Likert scale where score 1 & 5 depicts strongly disagree and strongly agree respectively. Research questions were designed in conformance with each of the variables so as to understand whether these variables have any relationship to each other in the form of independence – dependence framework.

Tools & Techniques to be used for data analysis:

The collected information was tabulated using SPSS and SPSS-AMOS statistical Package to perform Descriptive and inferential statistics including structural equation modelling (SEM) in order to understand interrelationship with varying intensity of all the variables which would yield significant impact on green product purchase behavior among the target segment. This has helped to interpret the extent of awareness and affinity of the target respondent and its implication towards purchase intention of green products.

Table - II

Two Stage Random Sampling Methods for choosing Educational institutes (Government and Private)					
Total no. of Institutions in the study region (Govt. & Private)	No. of Institution selected (First Stage)	Name of the Institutions Selected	Population of final year students in each institution selected	Sample selected form each Institutions (Second Stage)	Unit of sample as a Percentage of Population
Govt. – 08	2	GHSS - Ita	366	73	20%
		KV - 2	65	13	20%
Private - 10	2	Green Mount	250	25	10%
		King cup	109	12	10%
Govt. – 03	1	DNGC -02	836	84	10%
Private - 08	2	DBC	348	35	10%
		NENC	04	04	100%
Govt. – 3	1	RGU	660	102	15%
Private - 2	1	Himalaya University	552	52	10%
Total - 30	**09**		**3190**	**400**	**12.53 %**

Analysis & Interpretation

Analysis

Based on literature review and information collected from various dependable sources attempts were made to devise and indicative lists of green products which are being used or emerging in the market both for consumer and industrial purpose. Attempts were also made to make a working definition or a broad spectrum of conditions to consider green product.

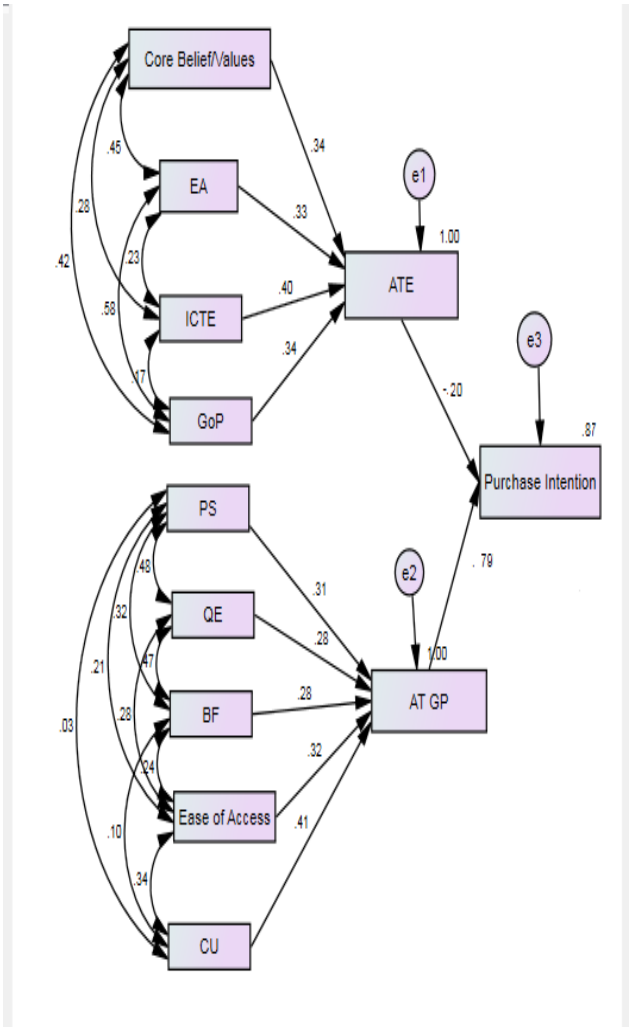
The concept of green product is vast and there is no single definition which can exhibit its spirits and essence in toto. The underlying presupposition is the green product is supposed to be the ultimate solution in the eyes of sustainability. The green product should confirm the following conditions:

a. It should be produced using green technology.
b. It should contribute least possible carbon emission and impacts on least depletion of ozone layer.
c. The products and its ingredient's should be mostly recyclable.
d. Follow the modern concept of circular economy.
e. Green products should be composed of nature based material rather a synthetic ingredients.
f. Ideally green products should have a definite and short life span and devoid of any chemical synthetic material and preservatives i.e. perishable in nature.

Table III

Example of Green products in different sectors	
FMCG	- Biodegradable Detergents - Soaps - Green tea - Eco friendly Disinfectants - All types of papers (writing papers, tissues, toilet)
Consumer Durability	- Recyclable batteries - LED light bulbs and tubes. - Solar panels - Clay based cutlery and crookery's
Health	- Biodegradable fittings & fixtures. - Cotton based consumables for dressing or bandit materials - Cotton bed sheet - Eco friendly disinfectants - Biodegradable gloves
White Goods	- Stacked washing machine and clothes dryer. - Gas fireplace. - Refrigerators. - Vacuum cleaner. - Electric water heater tank. - Small twin window fan.
Packaging material	- Edible package material like ice-cream cone. - Paper bags. - Tetra pack package
Transportation	- Bio fuel - Low carbon emission gas (CNG) - Recyclable tires

Sources: complied from https://www.conserve-energy-future.com/25-green-eco-friendly-products.php



From the above statistics it is evident that both 'attitude towards environment' and 'attitude towards green products' of respondent-consumer towards purchase intention for green products. However, the attitude towards green products of the respondent were found more significant i.e. 0.79. whereas for attitude towards environment the obtained value is 0.20.

The R^2 value is 0.87 which is highly significant and exhibit that the model is satisfied and justified by 87% of the data set.

The attitude towards green product (ATGP) is positively impacted by Price Sensitivity (PS), Quality Enhancement (QE), Brand Familiarity (BF), Ease of Access and Convenient to Use (CU).

ATGP ←======= PS = 0.31

ATGP ←======= QE = 0.28

ATGP ←======= BF = 0.28

ATGP ←======= Ease of Access = 0.32

ATGP ←======= CU = 0.41

Similarly Attitude towards Environment (ATE) positively influence by four independent variable viz. Core Belief/Values, Environment Awareness (EA), Individual Commitments towards Environment (ICTE) and Government Policies initiated towards Environment (GoP) .

ATE ←======= Core Belief/Values = 0.34

ATE ←======= EA = 0.32

ATE ←======= ICTE = 0.40

ATE ←======= GoP = 0.34

The statistics for determining model fit are enveloped below:

Sample Size= 400

Degree of Freedom= 40

CR > ± 1.96

P value= 0.000, Chi-Square value = 218.8

GFI = 0.818

RMSEA = 0.125

AGFI:

CFI = .779

NFI = .777

TLI =.735

Limitation of the study

The study was designed to capture relevant information from the sampled respondents who are studying in different institutions in the capital complex of the state of Arunachal Pradesh. This study could be extended to all other districts of Arunachal Pradesh to understand the level of awareness and affinity in the heterogeneous environment, geo-political factors and diversified cultural values and practices i.e. spread over across all the distinct major and minor tribe of the state. The study cannot be holistic and comprehensive in nature with the tantamount of cross-sectional data. However, it could be more effective if longitudinal data could be captured and analyzed. The study outcome could be more convincing if samples could be captured on regular interval following the stratified random sampling method. Since the concept of green product is apparently new in the region, the study might suffer from non-sampling errors. There is in need of Modification Indices as Chi-Square & RMSEA value is high. AGFI values are slightly lower.

Scope for further study

The study was conducted to understand the level of awareness and affinity among the young generation residing in a mountainous forest dominated state of north-eastern region which is somehow different from the tier-I and tier – II cities in regard to the lifestyle pattern, the level of consumerism. In fact the people at large in the region are more close to nature in the spectrum of biodiversity. The intention behind the study is to understand what extent the indigenous society is influenced by the ultra-modern lifestyle, hardcore consumerism with the advent of massive globalization leaving behind their core value and commitments towards nature. If these societies are aroused by the growing affinity towards usage of non-green products, it would be detrimental for the human civilization to sustain and survive. The study explicitly attempts to know the level of awareness among these population and whether such awareness essentially yield for developing higher purchase intention of green products or not. On the contrary, the study also focused on other cues of green products like price, ease of access, branding, ease of availability, quality enhancement and their possible impacts on purchase intention for green

products particularly in the indigenous community.

Recommendation

This study shows that respondent consumer of the region under study are more concerned towards Price Sensitivity (PS), Quality Enhancement (QE), Brand Familiarity (BF), Ease of Access and Convenient to Use (CU) which forms attitude of the consumer towards green products that essentially influence purchase intention towards green products. On the contrary independent variables like viz. Core Belief/Values, Environment Awareness (EA), Individual Commitments towards Environment (ICTE) and Government Policies initiated towards Environment (GoP) also impact collectively towards forming attitude towards environment (ATE) and that essentially influence Purchase Intention (PI) for Green Products. However ATE ←==== PI = 0.2 and ATGP ←===== PI = 0.79 respectively. This represents that among the respondent consumer there is a need of enhancing higher environmental awareness or commitments towards environment among the young population of the state. Since the target population mostly engaged in school, colleges and university, the academic institution must organized environmental awareness camp in the campus as well as through outreach programmes so that this could influence the young generation for enhancing higher purchase intention of Green Products. On the other hand the entire world is moving towards green movement which would definitely enhance the smaller markets with good quality and affordable green products with higher accessibility by the consumer across the country. Unless the awareness and commitment towards environment is firmly reinforces, the improvement in supply side would not achieve the desired results.

Conclusion

This study attempts to understand the views, observations and the sense of commitments of young educated respondents of a north eastern state. The underline spirit behind this study was to explore the level of penetration of green movement from mainland India to the remotest corner of the country particularly among the budding leaders of the future. This study prescribed that all the state and non-state stakeholders should design and delivered environment related campaign or dedicated illustrative module in the course curricula as a means of time bound and OOP action plan. The term development has been perhaps wrongly or narrowly manifested within the locus of massive infrastructure, construction, and building of engineering structures to jump

from natural green to jungles of concrete. The north eastern states are still alive with its flora and fauna. If the adoption of green products has not been incorporated by upcoming generations, the flood of indiscriminate and irresponsible consumerism would sweep the core values of sustainability for the region and for the entire nation.

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Chapter 14
QFD Approach for Integrated Information and Data Management Ecosystem: Umbrella Modelling Through Internet of Things

Arindam Chakrabarty and Tenzing Norbu

Abstract The journey of human civilization has been phenomenal and indeed multi-dimensional. It started with the struggle for existence, survival, growth, transformation and enrichment for gratifying physical as well as intellectual aspirations. Experiential knowledge system and scientific acumen had been the propeller of the engine of development which essentially began with the ignition of fire followed by the inventions of wheels and so on. With the growing complexities of life and multifaceted ambitions, the problems are becoming compounded which need to be solved by the interface of cognitive skills and technology. Triumph of human societies has crossed many milestones at different ages i.e., Stone Age, Bronze Age and Iron Age through evolutionary historical episodes like Paleolithic, Mesolithic and Neolithic era. The dynamics of contemporary human civilization solely depends on knowledge economy at the behest of the present information age. The impetus of information has been widely accepted and practiced across the horizontally and vertically integrated economic orientations worldwide. The degree of intensity and commitment might differ among various societies throughout the globe. The concept of Internet of Things (IoTs) has become popular among practitioners, academia and researchers as it acts as the idea of umbrella value proposition with the synergy of related multipliers. The growth trajectory for the advancement and welfare of human races primarily depends on the availability, accessibility and usability of data on multi-dimensional variables. In fact, efficient data management system has become the backbone of all the developmental models. The government agencies even the corporate sectors are also reciprocating to this call of the hour and collect data in accordance with their sectoral limitation. This is

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welcoming but not exhaustive since it suffers from inconsistencies manifolds. Now, the priority and thrust have been convoluted on the real time data rather being confined into mere collection and use of unintegrated raw data. This chapter would attempt to develop a model based on 'Quality Function Deployment (QFD)' approach using IoT platform to augment the real-life data management system which would interact and share between all the stakeholders conforming the spirit of selective data privacy and confidentiality. This would also strive to bring reforms in the existing process of planning, strategy formulation and project implementations.

Keywords QFD approach · Integrated information · Data Management Ecosystem · Umbrella Modelling · Internet of Things (IoTs) · Real-life data management system

14.1 Introduction

14.1.1 Genesis and Practice of IoT

The term Internet of Things dates back to the year 1999. Most of the sources believe that Kevin Ashton (Co-founder of MIT's Auto-ID Centre) is the one who coined the phrase "Internet of Things". However, the acronym IoT is deemed to be the later innovation. IoT is one of the burning topics in the IT world now. It is a network of physicals things embedded with software, microchip, sensor etc. which enables immediate access to information about the physical world thereby leads to improvement in efficiency and productivity. In a span of two decades, it has got widespread acceptance across the world.

14.1.2 Opportunities for IoT

The opportunities of IoT are enormous and ever increasing. The Business Insider projects around 24 billion IoT devices shall be installed by the end of 2020 [1]. However, the forecast of other researchers exceeds far ahead. Gartner projected around 25 billion devices by the same timeframe [2].

The IoT led ecosystem has been widely practiced in today economy and it is emerging with higher volumes in various sectors like Aerospace and Aviation, Automotive, Telecommunications, Medical and Healthcare Pharmaceutical, Retail, Logistics and Supply Chain Management, Manufacturing, Process, Transportation, Agriculture and Breeding, Media, Entertainment, Insurance, Mining etc. The Return on Investment (ROI) in IoT segment is projected to touch 13 trillion USD by 2025 [3].

It is predicted that more than half of spending on IoT sector may primarily focus on dedicated and customized manufacturing, transportation, logistics and utility services by 2020 which essentially portray that the future industry would be dominated by high-end transformative technologies [4].

14.1.3 Application of IoT

Over a period of time, IoT has emerged as an indispensable component for the development of every nation worldwide. It is being applied in diverse areas such as Smart Home, Wearable, Connected Cars, Industrial Internet, Smart Cities, Agriculture, Smart Retail, Energy Engagement, Healthcare, Poultry and Farming etc. Many industries like Healthcare, Transportation, Agriculture and Breeding, Media and Entertainment, Insurance, Recycling, to name a few, are increasingly using IoT [5]. Therefore, IoT intervention is inevitable in today's era to foster the growth of economy.

14.1.4 Information and Data Management Ecosystems: Experiences from India

The development of economy essentially relates to its resources, knowledge system, rate of creation of new knowledge and optimal sharing of knowledge and resources for making its dynamic and meaningful application. So, the focal point of supremacy in economic model depends on the sharing of information and knowledge system across the stakeholders to a large extent. In India, the state sponsored institutions including academia and research organizations have been creating high quality knowledge and various forms of information and databases regularly. But it suffers from comprehensive integration of all the knowledge and databases in a harmonious manner. As a result of that the India loses its quality and meaningful application. According to Global Entrepreneurship Index (GEI), 2018, India ranked 68th position out of 137 countries across the globe where India scored least in Technology Absorption (5%) followed by Networking (14%) and Cultural Support (14%) in order to understand the propensity of entrepreneurship in India from global standards [6]. This signifies that in general, India lacks in sharing knowledge and information that essentially has created least performance in absorbing technology from lab to market followed by its culture of creating integrated network or platform for sharing information.

Of late, the State Agencies are concentrating to create nationwide database network for example Shodh Ganga in India for Higher Education, INFLIBNET, various reports of Sample survey or Rounds of NSSO Working Groups etc. However, these attempts are miniscule in comparison to its overall demand.

The availability of integrated knowledge set, the ease of access and its effective use are the pre-requisites for scientific and economic development of the state. The transparency and disclosure of Private Sectors in India are not encouraging in general barring a few large firms. There are instances of dubious information and over-estimations of information revealed by the organizations. The concept of creating integrates and shareable Corporate Database is almost absent in India except miniscule attempts by a few agencies purely for commercial purposes.

14.1.5 Exploring Problems in Information and Data Management Ecosystems

The economy of developing nations is quite different from the developed ones. The firms in India are, in fact, sandwiched by various compelling forces and inhibiting factors. The dynamics of rapid technological advancement, bottlenecks like resource crunch, global competitions and turbulence in policy directions are the indicative examples of such antecedents. All the firms in India do not function on excelling their core competency for fetching higher growth. Many of them suffer from threat perception for their existence, survival and perpetuity. Under these circumstances; it may be suicidal for the firms to share all its information in the name of transparency or disclosure. So, India has become the victim of its inherent inconsistencies and challenges for creating integrated and shareable database system as compared to western world.

14.1.6 Concept of 'Quality Function Deployment' (QFD)

QFD can be referred as a system that attempts to translate the quality parameters of Product, Process and Services as a part of TQM initiative for achieving desired customer satisfaction.

14.1.7 Development of QFD Approach

The works of Akao describes that the QFD approach originated in Japan during late 60s of 20th Century [7]. The QFD initiative was first observed when the Oil Tanker was designed at the Kobe Shipyards of Japan in 1972. Mizuno also used this model to design customer satisfaction framework into a service offering encounter. In the mid of 80s of 20th Century, Don Clausing of MIT introduced this QFD as a design tool to the United States [8]. In fact, QFD is a strategic intervention to unify all the key areas so that the outcome of the process could be excelled and optimized.

14.1.8 QFD's Areas of Application

QFD is applied in diversified fields of application like Production, Product Design, Manufacturing, Information Technology (IT), Engineering, Research and Development (R&D) etc. [9] and other facets of life. It is well sought instrument that may be deployed in the organizational functions that are necessary to assure customer satisfaction which may include business, data management enabler/ ecosystem etc. It is also deployed to achieve quality improvement, its management and to foster 4IR (Fourth Industrial Revolution).

14.2 Review of Literature

14.2.1 QFD

Since 1966, QFD has been extensively practiced by the leading companies across the world [10]. In fact, it is expected that QFD will be considered as effective tool for quality assurance in the information age [10, 11]. In QFD process, it is important to know weights for the customer requirements so as to initiate actions accordingly [12]. For this, a fuzzy Analytic Hierarchy Process (AHP) using extent analysis was proposed to determine the same. Besides, Wasserman also introduced a Decision Model for the prioritization of design requirement during the QFD planning process [13].

14.2.2 Integrated Information and Data Management Ecosystem

Integrated Information System (IIS) can play a crucial role for effective management of agriculture and ecosystem [14]. It is a tool for trouble-shooting, decision making and knowledge management [15]. Also for issues like Climate Change and Environmental Monitoring and Management, IIS is highly essential [16]. Integrated approach can serve as a model for Resource and Environment Management in the coming days.

Lari proposed a model which he believes that the model can serve as a framework for Quality Information Management within organizations [17].

Hua and Herstein iterated that IIS is necessary for successful policy making for the development of education system as it ensures open communication, information sharing and information use [18].

Carlson et al. proposed a system called Integrated Business Environmental Information Management (IBEIM) which efficiently supports and integrates environmental information management for Environmental Management Systems

(EMS) tools, LCA and other environmental process modelling tools, and Design for Environment tools. Through this system, Information and reports can be handled efficiently by organizations regardless of size [19].

14.2.3 Internet of Things (IoT) and Its Application

IoT can be considered as a global network infrastructure composed of numerous connected devices that rely on sensory, communication, networking, and information processing technologies [20]. A foundational technology for IoT is the RFID technology, which allows microchips to transmit the identification information to a reader through wireless communication. By using RFID readers, people can identify, track, and monitor any objects attached with RFID tags automatically [21]. RFID has been widely used in logistics, pharmaceutical production, retailing, and supply chain management, since 1980s [22, 23]. Another foundational technology for IoT is the Wireless Sensor Networks (WSNs), which mainly use interconnected intelligent sensors to sense and monitoring. Its applications include environmental monitoring, healthcare monitoring, industrial monitoring, traffic monitoring, and so on [24, 25].

14.3 Objectives of the Study

(i) To study the importance of Integrated Information and Data Management Ecosystems.
(ii) To propose QFD enabled Umbrella Modelling for Integrated Information and Data Management process through IoT intervention.
(iii) To explore opportunities and challenges for implementing the model in Indian context.

14.4 Research Methodology

This paper is exploratory. The study is based on secondary information. It has been developed reviewing various research papers, reports and using relevant information.

14.5 Analysis and Interpretation

14.5.1 Analysis—I

The importance of Integrated Information and Data Management Ecosystems is enormous. Glimpses of indicative importance are noted below:

- There is lack cross-sectional data on various indicators catering to diversified domains. Even the data are not reliable and regularly published. This leads to inconsistencies in generating panel data.
- In India, there is need of real-time observations in most of the dimensions of economy. Another dimension is the available data set are not generated or published on same reference period. Now-a-days, high precision of real-life data is available that helps to make strategies projections/forecasting of weather conditions which can be shared for agriculture, fishermen working in the river and seas, agriculture practices etc. This minimises both loss of resources and loss of human and domesticated animals through strategic displacement or precautionary measures.
- Academicians, researchers and policy makers can formulate appropriate strategies for the emerging issues in terms of priorities of economy.
- Both the cross-sectional and panel data are helpful for designing both short-term and long-term policy planning in the form of e-governance, investment or implementation strategies. Cross-sectional data is for evaluating certain policy implementation activities.

From various studies, it is found that in spite of having positive relationship between the rate of corporate disclosure and transparency with the firms' net worth and profitability [26, 27] miniscule of firms and mostly the large firms have evidenced their efforts and commitments for corporate disclosure and transparency. The MSMEs are least interested in this area that results lesser confidence among all the stakeholders. On the contrary, the firms practicing higher order of Corporate Disclosure are sometimes questioned in terms of credibility and reliability of such information. The instance of Satyam, Enron, Lehman Brothers etc. are the testimony of such arguments where the firms desperately elevated and over projected the firm's net worth by creating fictitious assets. So, the quality, reliability and credibility of information disclosed by the firms are of paramount importance if the society is committed to have ethical practice and good governance (Fig. 14.1).

It is also important how fast the information has been collected by the firm. If the firm has to devise policies or strategies based on past data, it would be merely the 'System Approach' to management which can solve the problem on 'Reactive Mode'. In contrast to that if the firm is enabled with real-time data management system, the business entities may be strengthened with the ability to have 'Contingency Approach' to management that can 'stop the bleeding' instantly by divulging prospective and proactive mechanism. If the experiences and knowledge system (excepting the critical business secrecy) are shared and exchanged, the society would traverse with greater accomplishment and exposure to progress in the journey of excellence collectively with differentiated individual success story.

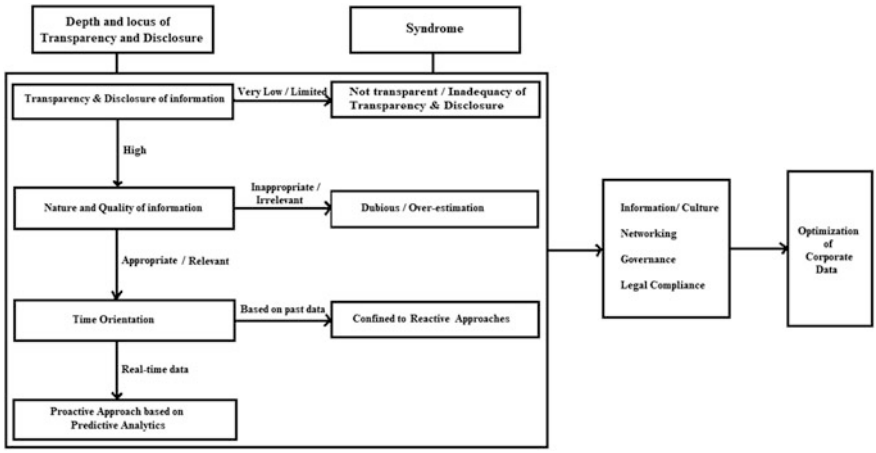
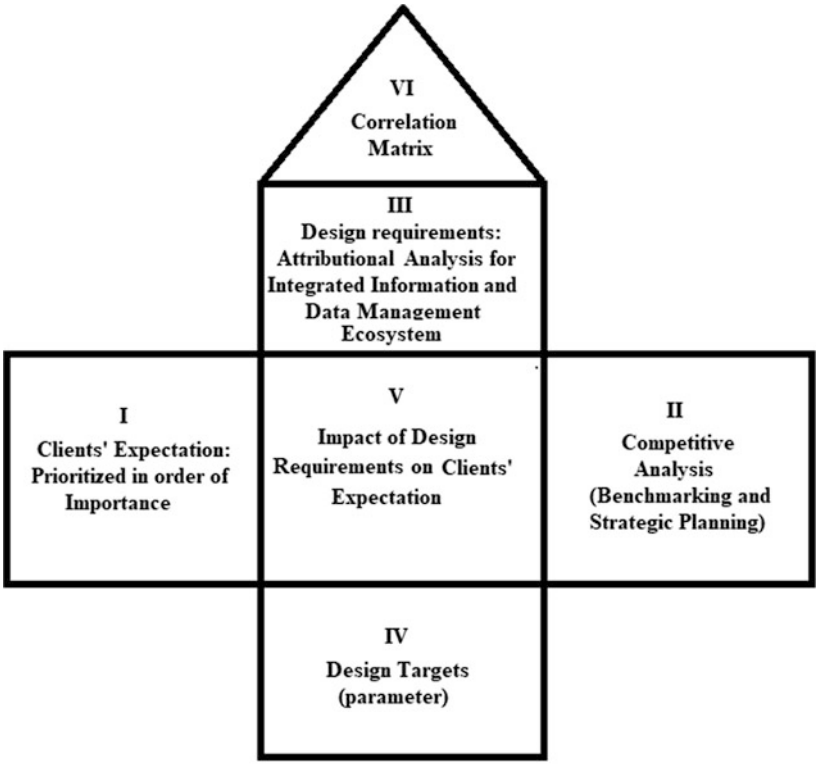


Fig. 14.1 Schematic diagram for rationalizing Integrated Information and Data Management Ecosystem. Developed by the Authors

The holistic development in the process of collectivism without diluting individual identity would have been the ultimate goal of effective and efficient Data Management Ecosystem. The degree of optimization of such process would determine the growth rate of Human Development Indicators. The 'Schematic Decision Box' has been depicted above to understand the depth and locus of Transparency and Disclosure that essentially prescribes for effective and efficient Integrated Information and Data Management Ecosystem.

14.5.2 Analysis—II

Abundance reserve of information and its on-time accessibility may be deemed as the most precious resource in the knowledge economy. The 4IR has empowered the society with the application of IoT that can be guided by developing Non-Human Intelligence through continuous Machine Learning (ML) protocol. The 4IR era enables the system that can interact with each other and analyse big quantum of data which may be collected on real-time basis. It is the high time to integrate and incorporate all the functional KRAs (Key Result Areas) that need to be blended to form a comprehensive ecosystem with the intervention of IoT infrastructure. The functional KRAs are to be embodied in the spirit of Quality Function Deployment (QFD).



House of Quality

The basic structure of QFD as explained in above figure essentially depicts how the QFD system operates in consonance with the voice of customer and the voice of organization divulging the spirit of Competitive Analysis. The relationship matrix helps to identify the designed targets.

The proposed model indicatively may comprise of the following functional KRAs (Fig. 14.2):

- **Real-time Information Recording System**: The devised framework would be able to collect record and retrieve all sort of valued information including research outcomes in the form of formula, copyright or patent etc., on real-time basis with the exposure of IoT led ecosystem.
- **Information Security Protocol and Client-Server Architecture:** The proposed model would instil appropriate Information Security Protocol so that the database would not corrupt or lose due to any malware attack. The system should have high precision 'Client-Server Architecture' so that it ensures free flow of data without any redundancy unless strategically entangled with limited access.
- **Interactive Protocol to develop Artificial Intelligence (AI) and Machine Learning (ML)**: The designed framework would conceptually be reinforced in

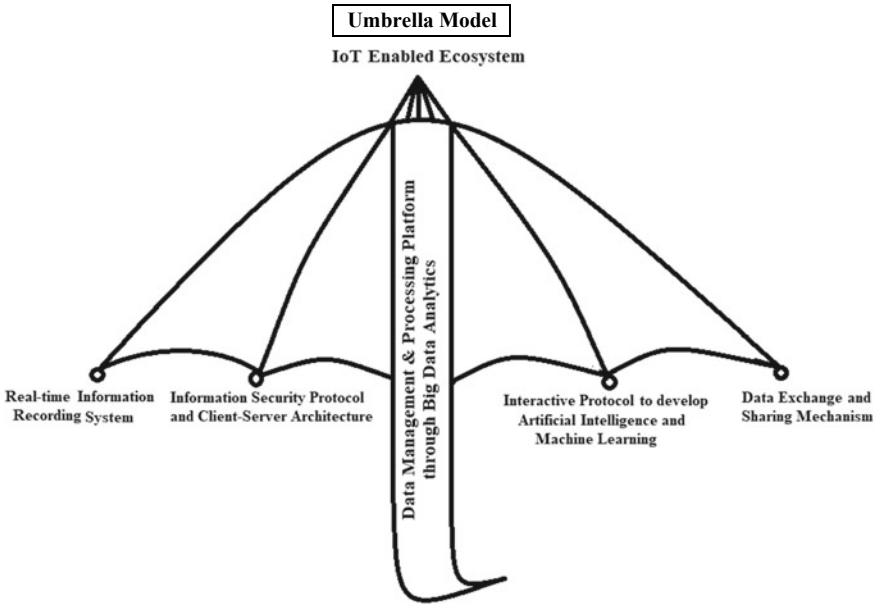


Fig. 14.2 QFD approach for Integrated Information and Data Management Ecosystem: Umbrella Model. Developed by the Authors

such a fashion that the various entities interact with each other at the fullest synergy of permutations and combinations to retrieve meaningful indications/ predictions. The system may be allowed to expose with AI augmented with continuous ML exercises.

- **Data Exchange and Sharing Mechanism**: The purpose of this model is to ensure that all the clients should be able to access, share and exchange the information at the fullest of capacity. This functional KRA would enable to optimise the essence of coordination, consolidation and collaboration among all the stakeholders with the optimum utilization of effective and efficient Data Management System.
- **Data Management and Processing Platform through Big-Data Analytics**: All these KRAs would converge to experience real-time and meaningful interpretation so that the broader dimension of Big-Data Analytics i.e., Descriptive, Predictive and Prescriptive could be achieved holistically for the dynamic problems emerged into the real-life situation. All these competing priorities could be manifested as a fusion of Umbrella Modelling as presented below.

In fact, the QFD approach is of paramount importance in designing an Integrated Information and Data Management Ecosystem. The Quality Functions or the KRAs are to be identified, strengthened and the dynamic form of interactions among the KRAs would create Non-human Intelligence.

14.5.3 Analysis—III

14.5.3.1 Opportunities

The Integrated Information and Data Management Ecosystem has enormous demand for transforming India in terms of economic development, R& D and all other Value Chain functions. The state has concentrated to excel its data infrastructure particularly at the pretext of 4IR. The Union Ministry of Company Affairs, India recently announced to incorporate AI into MCA21 e-Governance service which will make compliance and registration procedures easier. Moreover, it can play a vital role in resolving conflicts as well [28]. The indicative Opportunity Matrix for this Data Revolution System may be identified as follows:

i. Mobile penetration and internet access have been increasing in an incremental rate in India and Mobile Internet has become the pioneer in the access of internet service across the nation. The popularity of Direct Benefit Transfer (DBT) through Aadhar-based Biometric Smart Card has proved successful in Andhra Pradesh [29]. The Integrated Information and Data Management Ecosystem may lead to a massive transformation in the lives and economy of the regions which are remote and away from the central developmental trajectory.
ii. There is a growing trend for emphasizing on Corporate Disclosure in the country which may create gigantic opportunities for comprehensive Data Management System.
iii. In government system, RTI Act 2005 has opened and introduced the process of compulsory information flow on demand of every citizen of the nation. Thus, the Act enforces the government departments to collect, preserve and disseminates the information. However, there is no such Act for Corporate Bodies. The Integrated Information and Data Management Ecosystem would enable to synthesize all sorts of data that necessarily include the basic information of the corporate without intervening the key issues like Patent, Copyright, Business/Trade Secrets etc.
iv. The growing popularity, adaptability and application of IoT have mesmerized the academician researchers and even the users of young generations which essentially creates a platform for sharing multiple and high magnitude of dataset in the public domain or open access forum. If the valuable information is integrated, this could lead the society with fascinating experience and illuminating features.
v. Cutting-edge research depends on the voracity, quality and reliability of dataset and its continuum of data flow. This Pull Strategy would promote the culture and capacity for creating such high-end data infrastructure in the India and across the globe.

14.5.3.2 Challenges

In any study or research, the Opportunity Matrix determines the ease and expectancy mode of any model. But the future expectancy constructs must be complemented and supported by continuous form of tangible and intangible resources. One of the most vibrant factors may be the role of users and the commoners to make it successful. In Indian context, there are few indicative challenges or rather constraints that need to overcome. A subset of challenges are highlighted below:

i. The country suffers from the lack of infrastructure facilities. As 68% of Indians rest in villages [30], it is difficult to bring them in the ambit of the sophisticated and high-end Data Management Ecosystem unless equitable infrastructural development takes place. However, it requires huge investment of financial resources. It is up to the nation to decide on the competitive priorities, that is, what extent the government is committed to value the essence and aspirations of developing Integrated Information and Data Management Ecosystem. Even if all the state and non-actors are unanimous to achieve such landmark, it is practically impossible to develop equitable infrastructure across Pan India within a smaller time frame. The government has been taking initiative consistently. The hallmark of 'Bharat Nirman (2005–09)' initiatives were witnessed to develop the rural infrastructure primarily in irrigation, roads, housing, water supply, electrification and rural telephony [29]. The trend has been fuelled and continued by subsequent governments through their various policy interventions.
ii. India still suffers from adequate competency on a single language platform as it is difficult for the multi-lingual society to learn and practice on English language. The proposed Data Management System may be useful if majority of Indians can read and understand in English language.
iii. The initial investment of such prototype or framework is associated with high cost implementation and that needs to be absorbed by the state and non-state multi-stakeholders.

14.6 Recommendations

The paper has demonstrated how the historical data as well as real-life information and knowledge system can be recorded, preserved, accessed and optimized so that every stakeholder of economy may excel in a mutually benefitting and collaborative manner. The development of 4IR has created enormous opportunity and genuine demand for creating dynamic database infrastructure which would be expected to interact arbitrarily as a form of AI. The implication of this paper may be conceived with the notion how the various forms and facets of data platform can be conjugated, integrated and inter-linked to create an Umbrella-shaped morphology.

14.7 Limitation of the Study

The study intends to formulate a dedicated model for integrating Information and Data Management Infrastructure based on available research inputs and existing frameworks. The model needs to be implemented in a test region i.e., a small district or sub-division where the robustness of the model may be verified. The emerging attributes or concerns during this experimentation process may be explored, identified and incorporated with the existing model framework. Thus, the information ecosystem can be strengthened through continuous development process. However, the model has not been trialled as its present form.

14.8 Conclusion

The world has been progressing through information age where big data analytics has become prolific leader of the millennium. The synergy and synthesis of Artificial Intelligence (AI) based on both panel data and real-life information is the future of our society. The transition and transformation of new generation technology and scientific application essentially depends on the momentum, magnitude and the quality of data storing, preservation, analysis and interaction process through experiential learning and QFD of all the attributes and entities. The fusion of such heterogeneous modalities in a most coherent framework for achieving Integrated Information and Data Management Ecosystem has become the call of the day which needs to be augmented both for developing and developed nations.

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Mission SDGs Through Food Waste Management: Nature and Approaches

Arindam Chakrabarty and Uday Sankar Das

Abstract The global fraternity has been embarrassed to understand how to feed the elephantine population of this planet. The greed of comfort, convenience, and technology ecosystem has mesmerized our life in such a fashion that the human society has been up-rooted from the nature. The wave of infrastructure development results in heavy encroachment of fertile land as well as yielding to regressive fertility of land. On the contrary, the society has not learned to optimize the utilization of resources whatever forms it may be. These compel the United Nations to formulate specific target-oriented Sustainable Development Goals that need to be achieved by 2030. Food waste is still a menace of mankind. It may be of many forms and dimensions. Food waste exists in every phase of supply chain. Most surprisingly, the stigma of this menace reaches to our household also. The irony of life is that, on one hand, we are habituated to accept that wastage in foodstuff as part of our livelihood, and on the other hand, the United Nations reveals its concern for poverty, hunger, and many other unaccomplished goals. The world is now on the verge of Fourth Industrial Revolution. The IoT-based ecosystem has been emerged as an inseparable entity of the modern societies. This paper has attempted to assess and account the loss of economy for wastage of food items from global canvas to national perspective. This study has also focused on how to use IoT platform so that the food wastage can be reduced up to a considerable amount both in the supply chain and even in household practices. This research work is based on secondary information like research papers, reports, and results of other relevant studies. The paper has attempted to develop and devise a conceptual and strategic model where the IoT ecosystem can be incorporated to ensure real-time solutions and to curb on massive food wastage practices. If the model is implemented and practiced with appropriate case specific modifications

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and customizations, it would make the economy more efficient and address different perspectives and dimensions of UN Sustainable Development Goals (UNSDGs) to a larger extent primarily in Indian Context.

Keywords Food waste management · Supply chain · Fourth Industrial Revolution IoT ecosystem · UNSDGs · India

1 Introduction

The journey of human civilization started with the ignition of fire, invention of wheels, and creations of indigenous tools and techniques through the passage of various ages. Today, we are in the age of information automation and moving toward Fourth Industrial Revolution. The success of our human civilization is based on key primary needs, i.e., food, clothing, and shelter. However, this is the irony of life that in spite of achieving various developmental indicators, the human society is still unable to fulfill the basic needs like food which is reflected in various literatures, research outcomes and from the experiences of reality. To cater the critical issues, the United Nations move ahead from achieving Millennium Development Goals (MDGs) to Sustainable Development Goals (SDGs) where poverty and hunger were given primary thrust.

1.1 Food Waste Across the Globe

Around 1.3 billion tonnes of food produced gets wasted globally which account to around one third of the food produced. A whopping US$680 billion and US$310 billion are lost in the industrialized countries and developing countries, respectively. A 670 and 630 million tonnes of food are wasted for industrialized countries and developing countries. Perishable items like fruits and vegetables account for the highest losses post-harvest. Food loss and food waste per year are roughly account to 20% of oilseeds, 35% for combined for meat, dairy and fish, 30% for cereals, and 40–50% for root crops. Per capita food lost or wasted every year is between 95 and 115 kg/year in Europe and North America. While 6–11 kg a year is wasted in countries of South-Eastern Asia and sub-Saharan Africa. A 40% loss of food items occur at post-harvest or at processing level in developing nations, and same amount is lost at retail and consumer levels in industrialized nations (Table 1; Fig. 1).

Table 1 Per capita food losses and waste (kg/per year), at consumption and pre-consumptions stages, in different regions [1]

Region	Production to retailing	Consumer
Europe	187	94
North America and Oceania	181	115
Industrialized Asia	165	70
Sub-Saharan Africa	159	7
North Africa, West and Central Asia	181	31
South and Southeast Asia	115	13
Latin America	198	24

Adapted from key finding of Food and Agriculture Organization of the United Nations

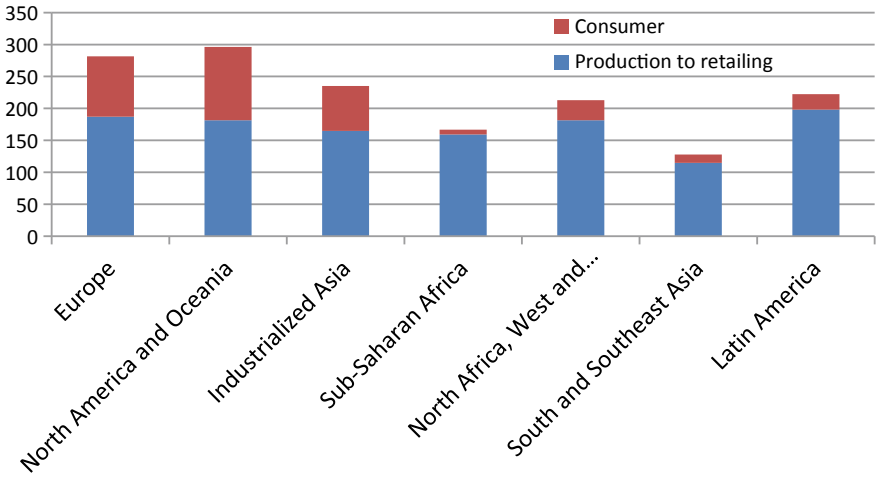

Fig. 1 Per capita food losses and waste (kg/per year), at consumption and pre-consumptions stages, in different regions (adapted from key finding of Food and Agriculture Organization of the United Nations) [2]

1.2 Food Waste in India

India has adorned the developing nation tag since the dawn of independence and is at the frontiers of food loss and food waste. India is ranked at 103 in the latest Global Hunger Index [3] report published in 2018 while a large section of the population still live below poverty line (21.92% of the total population as per RBI data published on Sep 16, 2015) [4] bureaucratic loopholes and intentional ignorance towards the issue has kept the problem alive till date. FCI, a premier food distribution corporation and a state owned utility is yet to fix the grain drain problem. It is reflected in numerous news reports that the food loss by FCI was in the tune of 1.94 lakh MT food grain that had been wasted between 2005–2013 [5]. Apart from this, India still lacks organized

cold storage facilities or processing plants within proximity of farmers producing perishable food items like fruits and vegetables.

1.3 Socio-economic Impact of Food Waste in the Context of Sustainable Development Goal

The Global Hunger Index [3] of 2018 point a staggering 124 million people across the globe suffer from acute hunger due to malnutrition, internal displacement, refugee status and poverty. Four of the total 17 goals prescribed by the United Nations SDGs focus on Poverty, Hunger, Good health and wellbeing, and responsible consumption and production (Goal 1: No poverty; Goal 2: Zero hunger; Goal 3: Good health and well-being; Goal 12: Responsible consumption and production). Food loss [6] is the primary reasons why most of the developing world still suffers from malnutrition and hunger which is caused by poor storage and processing in the post production phase and developed nations are highest contributor towards food waste [6] due to fast pace life, irresponsible and ignorant behavior towards the issue. While the former can be solved by application of technology and infrastructure management the later can be solved by improving upon the social physiological behaviors of the masses.

1.4 Introduction to Fourth Industrial Revolution

The term Fourth Industrial Revolution or 4IR [7] was coined by Professor Klaus Schwab, founder and executive chairman of the World Economic Forum in his book "The Fourth Industrial Revolution" based on the technologies of the artificial intelligence, machine learning, quantum computing, 3D printing, and the IoT. Around the year 1760, First Industrial Revolution started in Great Britain, which was powered by the invention of steam engines. Almost a century later, Second Industrial revolution started which was characterized by mass production (from craft-oriented production to mass production) in various industries like steel, oil, and electric. Some of the greatest inventions like internal combustion engine and light bulb came through in the same period. The Third Industrial Revolution or "The Digital Revolution" started somewhere around 1960s powered by the greatest inventions of the century, semiconductor chips, which gave rise to personal computing and eventuality made the Internet a real possibility. Now, 4IR is knocking on the doorsteps of humanity which will eventually change the way we eat, live, think, or nearly everything we do to sustain our life.

2 Literature Review

The unprecedented developments in the fields of digital, physical, biological technology are the three major drivers of the Fourth Industrial Revolution. There is an attempt to understand the impact of these technologies on various global, industrial, economic, and social developments [8].

One quarter of the food supplied for human consumption is wasted across the food supply chain. High-income countries generate food waste at all levels including household which is the highest. The study gathers data from 1062 Danish respondent measuring the intention and attitude not to waste food. Food waste can be controlled by making perceived behavioral control [9].

Sustainable Development Goals (SDGs) are successor of Millennium Development Goals (MDGs). It proposes 17 goals with 169 targets with numerous indicators [10].

Large-scale food waste in the global food supply chain has attracted attention due to its environmental, social, and economic impacts. There has been an attempt to understand the difference between food surplus, avoidable and unavoidable food waste by various specialist, to manage the waste, and to identify the most appropriate mechanism to create a sustainable supply chain management. There is also an attempt to understand and distribute the food surplus to poor people or to convert it as an animal feed [11].

The UN organization, Food and Agriculture Organization estimates a 32 percent loss of food produce in 2009 based on weight while a 24 percent in terms of calorie. Food wastage has negative impact on economy, and it represents a wasted investment, consumer expenses, and farmers' income loss. While food loss refers to losses incurred due to spills and spoils, food waste refers to losses due to infrastructure limitations or post-consumer waste which is generally fit for consumption. Food waste is generally a conscious decision to throw away the food [12].

Wireless sensor network (WSN) surrounds all living beings in the modern era and influences day to day living. A communication between all these wireless-enabled network creates the Internet of Things (IoT) to form a seamless environment to create a common operating picture (COP). The IoT has evolved from the static web2 (social networking web) to web3 (ubiquitous computing web) increasing the data demand [13].

Continuous population growth will keep a continuous demand for food supply for another 40 years approximately, while there will be a decrease in the capacity to produce food due to overexploitation of land and other natural resources including a threat from climate change. However, a more efficient ways of food production can be explored [14].

In order to feed the nine billion human populations by 2050, a review of food waste in the global supply chain is discussed. Data of post-harvest losses of grains are outdated, and current global losses are unknown. The impacts of food waste in the development of BRIC economies are also unknown while developing nations face food wastage post-harvest due to its perishability developed countries contribute to

high post-consumer food wastage which suggest a scope for behavioral change to reduce wastage in affluent population [15].

There is an attempt to understand the link between inflation in food prices and riots or food riots. Demonstrators of the riot pointed political repression injustice and inequality which mobilized and bought together various political coalitions to promote human dignity [16].

Electronic nose has been a trending technology for the last two decades largely due to numerous applications built around the sensors. Recent changes in the computing power have given the electronic nose a new possibility of various applications. It has provided a numerous benefits in the fields of biomedical, agricultural, environmental, food, cosmetics, manufacturing, military, pharmaceutical, and various scientific researches. Now, electronic noses can monitor all phases of industrial manufacturing [17].

An introduction to radio frequency identification systems and their strength, weaknesses along with deployment challenges is discussed along with various extensions that offer read/write memory and environmental sensing along with social issues [18].

Electronic noses (e-noses) are sensors that can detect various volatile organic compounds. A wide range of applications can be designed based on pattern recognition with the help of artificial intelligence or neural network. The future trend of the sensors is also explored [19].

3 Objectives of the Study

1. To explore varied forms of agriculture food loss at different stages up to the phase of consumption.
2. To provide an IoT-based solution for reducing food waste to a considerable amount primarily in closed system or household condition.

4 Research Methodology

This paper has attempted to understand, study food waste and its impact in the global context, provide solution through existing technological framework (IoT and electronic nose), and achieve related SDGs. This paper has been developed using secondary information collected from various relevant sources and documents. The paper has focused on how a technological solution would help achieve sustainable development goals of the United Nations by 2030.

5 Analysis and Interpretation

Analysis I

The various forms of agricultural food loss can be expressed by using the flow chart diagram as mentioned below.

Loss of Agricultural Produce at Farming Stage

- Agriculture food loss starts at the very beginning when farmers produce crop without adequate planning and sharing information among the producer's community and other stakeholders, and as a result of that, food loss occurs with overproduction of crops [20].
- Farmers harvest their crop prematurely for his personal consumption or to earn money. This accounts both the economic and nutritional loss of food grains [20].
- Massive use of pesticides and fertilizers diminishes the nutritional value of the food grains, and at times, it could be deterrent to human life.

Loss of Agricultural Produce at Transportation/Supply Chain

- During the movement of crops or food grains from field to warehouse or market, there are several supply chain/transportations loopholes like lack of refrigeration system, using FIFO technique or VED analysis (Valuable, Essential, and Desirable) (Fig. 2).

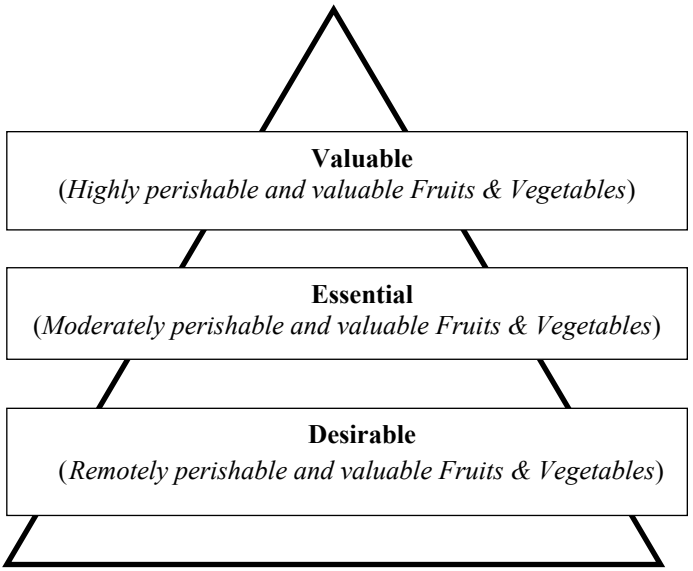

Fig. 2 Schematic diagram of application of VED analysis

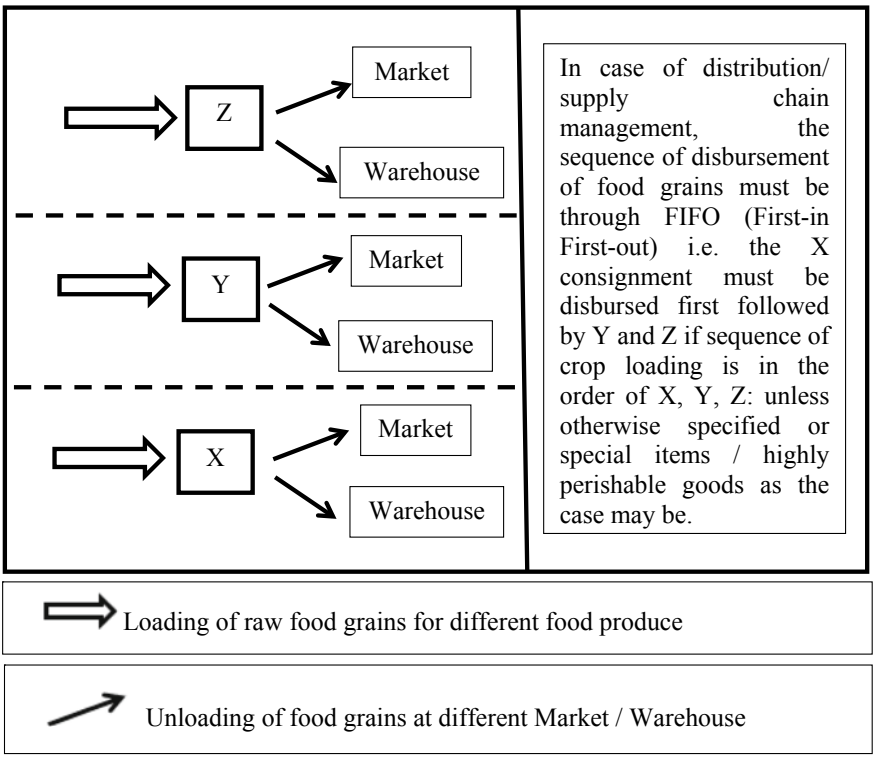

Fig. 3 Schematic diagram: application of FIFO method

Loss of Agricultural Produce at Warehouse/Cold Storage

See Fig. 3.

Loss of Agricultural Produce at Market Place

- In course of selling of food grains in the market, it is difficult to predict actual demand for each variety of food grains or crops. As a result of that, there is substantial loss of food grains in the market places which could not be sold at all or may be sold at a tendered expiry mode.
- In fact, accurate demand forecasting for every set of crops is next to impossible due to uncertainty of market dynamics and impulse purchasing behavior of the consumer.
- Lack of adequate refrigeration and cold storage system.
- Lack of Warehouse facilities.
- Due to excessive overproduction of crops, it results in higher storing cost and stagnation of crops which yield loss of food value, nutrition, and economy (Fig. 4).

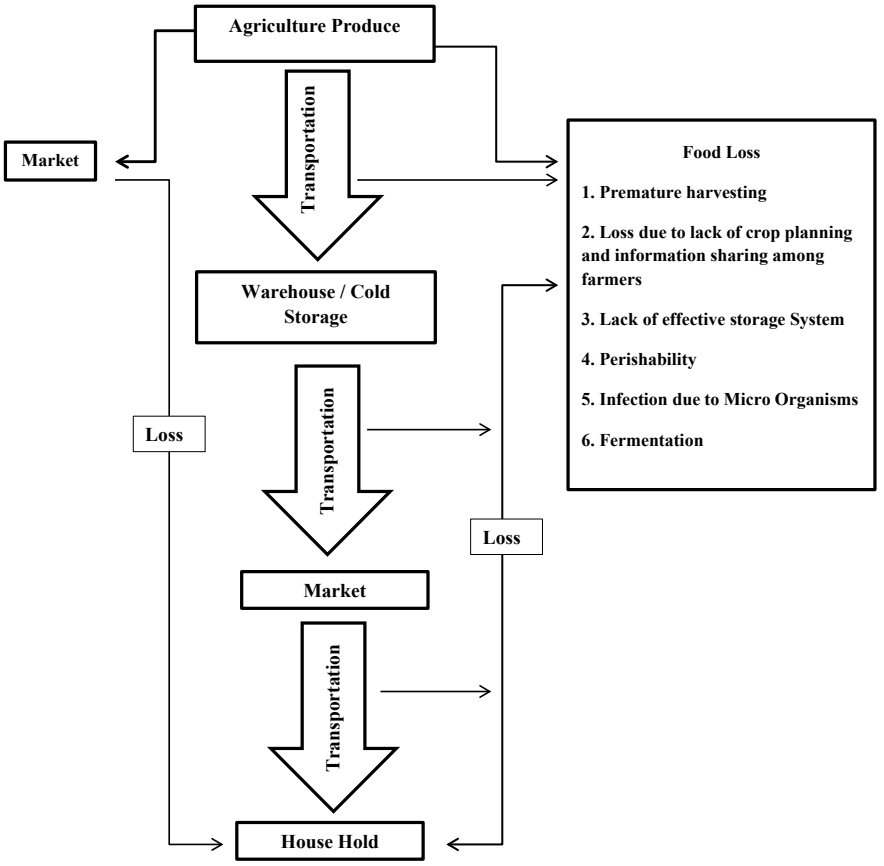

Fig. 4 Schematic diagram of food wastes at various stages

Loss of Agricultural Produce at Household

- Various ways of food waste take place at the household level both in uncooked and cooked format.
- The loss of uncooked produce is primarily because of oversupply of vegetables or food grains due to lack of ready information about the food reserves in the household. From lower middle class and above category, the family depends on household refrigerators for the purpose of preservation of food grains, vegetables, etc.
- The loss of cooked food occurs due to overestimation of perceived demand of food for day to day domestic consumption. This loss can be managed by experiential learning of the household and commitment of the members toward sustainable use of resources.

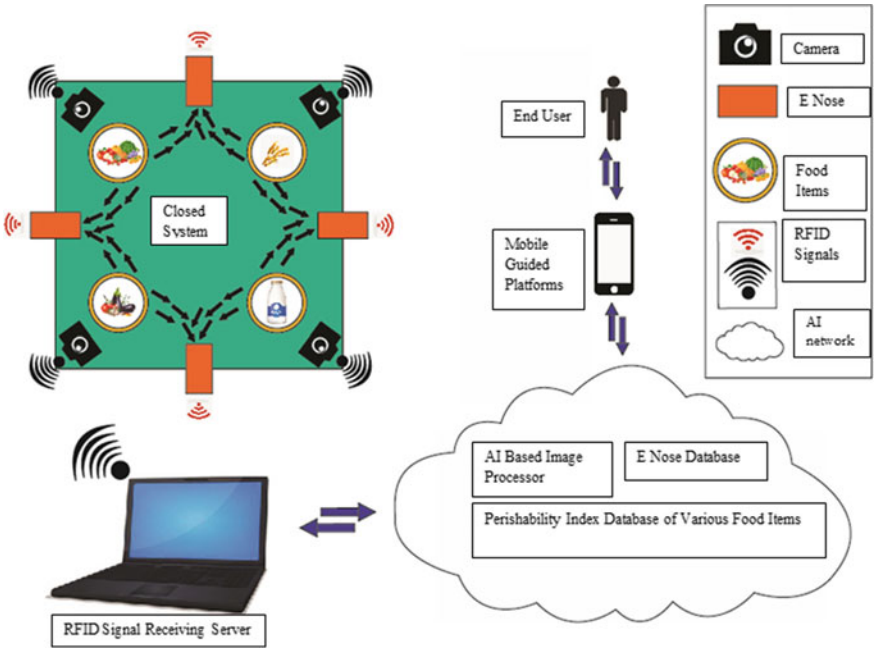

Fig. 5 IOT-based solution for reducing food waste primarily in closed system or household condition

- In fact, the loss of uncooked produce at the household level may be solved with appropriate smart in-house storage system and economic usage mechanism led by IoT intervention.

Analysis II

See Fig. 5.

Indicative algorithm for the model

1. The confined storage system (e.g., household refrigerator) needs to be augmented by multiple IoT devices that would act as E-Nose and E-iris as a means of sensory devices.
2. The IoT, E-nose and E-Iris would be provide adequate database for image processing for with pigment support (e-iris) and aromatic database (e-nose) on each specific food grains and vegetables generally stored in the system.
3. The sensory device will receive appropriate stimuli both aromatic and pigment and that would process using IoT, intelligence system (AI) by matching the preset database and finally the system would generate its predictive analytics about the nature of food produce stored in the system.
4. The processed results would be transferred at all the connected portals with the IoT ecosystem on real-time basis so that the user can be aware of the quantity and quality of each of the variants food products.

5. Based on this input, the user can take most appropriate purchase decision for further procurement of food grains, i.e., the set of variants to procure or not to procure and at what quantity. This real-time information would enable the household to prioritize which vegetables to cook immediately on priority basis in order to minimize both the nutritional and economic losses.

6 Conclusion

Food waste management has multiple implications on society as well as its economy. The world is highly apprehensive on the issues of food security, fertility of land, and nutritional benefits for upbringing off the human civilization. The sustainable development goals firmly advocate that poverty, hunger, and responsible production and consumption are the few integral dimensions which need to be improved if the world would like to achieve the essence of sustainability. Whatever the policy is formulated at macro level, finally the success depends on what extent it has been implemented and practiced at the very micro household level. This paper has emphasized on developing a sustainable solution to address the food loss issues at the household level with the intervention of IoT led smart technology.

Limitation of the Study

This paper has designed and developed a strategic solution in order to combat household syndrome. However, if the model is efficiently implemented, the degree of minimization of food loss could be explored so that the impact of the model could be studied, and necessary improvement on the structural morphology could be incorporated.

Working definition:

e-nose: An electronic nose is used to identify odors by detecting the "fingerprint" of a chemical compound using pattern recognition software [21].

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Dynamics of Knowledge Management in 4IR Through HR Interventions: Conceptual Framework

Arindam Chakrabarty and Uday Sankar Das

Abstract The world economy has been remaining captive to the exponential growth of knowledge. The concept of knowledge is diversified and multidimensional which essentially includes theoretical constructs, experiential learning, incepts of laboratory results, models and of course its ability to adapt changes. In fact, knowledge economy should be ideally the fusion of indigenous belief and practice and transformation of scientific know-how. The world has witnessed rapid transformation both in society knowledge system and industrial revolution. The twenty-first century has emerged as the torchbearer for fourth industrial revolution which can manifested in designing machines, gadgets that can be embraced with auto-guided instructions, artificially par excellence with human intelligence. The aspiration of fourth industrial revolution (4IR) demands higher order of knowledge, big data analytics and continuous improvement in R&D outcomes. So, it has become emergent to concentrate on the threshold level of knowledge management practices in the transforming economy. This paper has focused on how the interrelations among the level of industrial revolution, knowledge management and transformational HRM practices include KASH protocol using conceptual modelling.

Keywords Knowledge management · 4IR · Human intelligence · Transformational HRM practices

1 Introduction

The progression of knowledge management has been carried away through a long journey. The organization began to understand that human being cannot be compared with machine as a part of neoclassical theory of management. In the beginning of

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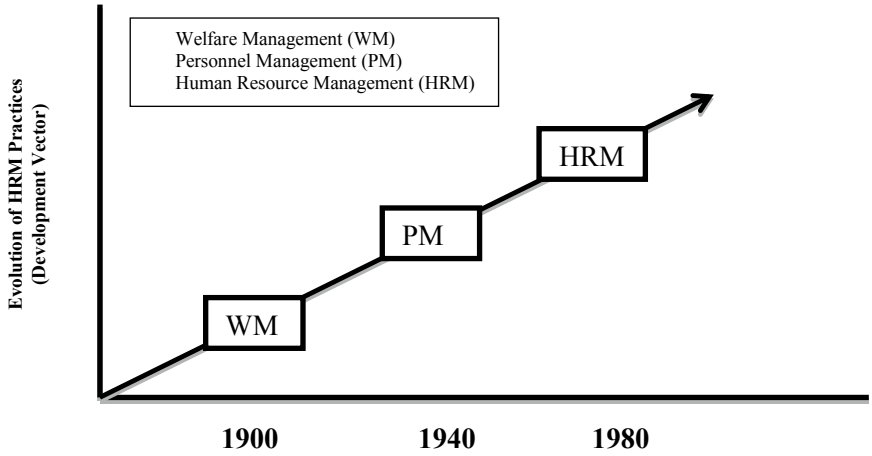
twentieth century, the concept of welfare management had been practised by few organizations which paid a special attention on the welfare measures of workers in the factory, but the experience of welfare management practices had not been complacent as it was desired. Prior to the Second World War, the idea of personal management emerged roughly in 1940s which concentrated on measuring performance of labour on various scales, even though this school of thought never recognized the labour as human resource. The importance of training development OD interventions organizational culture climate had not been given due weightage. From 1980, the organization started to implement human resource management over throwing the erstwhile mechanistic and dogmatic view of management. HRM has been evolved as an organic orientation that recognizes and respects labour force as a dynamic resource that can be appreciated over the period of time with the augmentation of knowledge, skill and experiences. The twenty-first century has revolutionized with the advent of superior level of technological advancement. The knowledge-driven economy has been witnessing with a new paradigm, i.e. generation of new idea, product, process, with the succession of high rate of obsolescence. It becomes faster as we proceed towards the present time.



Adapted & Modified from [1, 11, 13]

With the advent, progression and popularity of 4IR, the organizations have explored to recognize the imperative of knowledge management practices at the beginning of twenty-first century. This brings the accumulation of vivid information robust technology and big data compounded with the application of AI, ML and block chain technology, etc. Today, the construct of knowledge management is not confined in accumulating functional super specializations rather it has extended to endless interactions among various dataset from various domains in a multi-varied assortment of knowledge basket with multi-criteria decision-making (MCDM) protocol [14]. This envisages numerous innovative opportunities and new directions that lead to explore knowledge-led dynamic problem-solving mechanism.

1.1 Evolution and Understanding of Knowledge Management

Contemporary business writings have extensively focused on knowledge management and have curated it as a contemporary theoretical discipline and shifted the focus of organizations from tangible products and goods to intangible assets focused on performance and profitability in this competitive environment. Knowledge management has opened up the opportunity to add renewed strategic growth in any business organization [2]. A study 'Emerging Practices in Knowledge Management' conducted by the American Productivity and Quality Center of the USA points out six key strategies of a firm for practice of knowledge management (KM). From a business strategy point of view

1. As a tool to transfer best practices.
2. As a customer-oriented tool.
3. As discipline for personal development.
4. As a tool for intellectual assets management.
5. As a tool for knowledge creation and innovation.

Prominent fortune 500 companies like 'Dow Chemicals' and 'Texas Instruments' were also a part of this survey [6]. KM focuses on gathering of useful knowledge or for the business process so that the employees can readily access knowledge. It also helps to secure specified well-defined set of knowledge practice by preventing from use of inappropriate knowledge. KM is research intensive and involves application of organizational learning capacity over competitive advantage in the long run. Evolution of KM intervention can be categorized into six broad stages which can be further rationalized as depicted below.

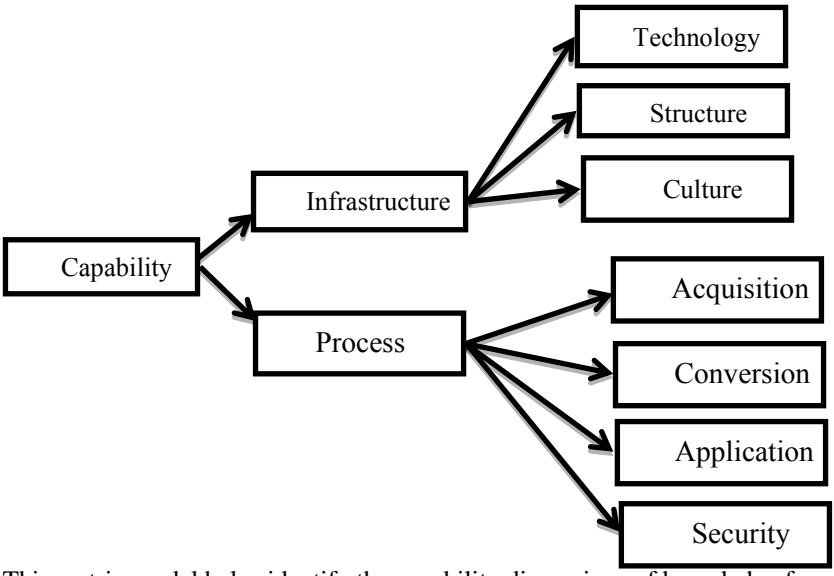
Six broad stages	Rationalization of stages
Initiation	KM initiation
Adoption	
Pilot implementation	
Organic growth	KM development
Organizational implementation	
Diffusion	KM maturity

The factors determining the evolution of KM are classified into knowledge self-efficiency, open communication and mutual benefits [4]. The example of companies like Dow Chemicals which is a treasure trove of unorganized intellectual property, whose main business is to earn royalty through licensing of technology and information highlights the importance and needs of knowledge management in order to organize this other wile piled up disorganized knowledge for profit maximization [6].

1.2 Dimensions of Knowledge Management

The knowledge management can be referred in two perspectives, i.e. in terms of capability dimensions and quality ontology. The capability dimension can be broadly categorized into two sub-dimensions, i.e. infrastructure and process. The attributes of infrastructure may include technological led ecosystem, other resources and support facilities structure, culture. The process matrix may comprise acquisition, conversion, application and security. This has been illustrated in the figure mentioned below:

Capability dimensions	Attributes	Meaning
Infrastructure	Technology Structure Culture	Organize fragmented knowledge in an organization Leverage of technological architecture Encouragement of employee interaction
Process	Acquisition Conversion Application Security	KM process of knowledge acquisition Utilization of the existing knowledge Application of knowledge Knowledge protection



This matrix model helps identify the capability dimensions of knowledge framework and its subsequent branch entities [3]. A conceptual frame work is proposed to manage the quality dimensions of KMS based on the environmental factors and its effects on the same. The resultant framework consists of 36 items grouped into the eight dimensions of KM namely Functionality, Completeness, Reliability, Usability, Access, Serviceability, Flexibility, Security [7, 9].

1.3 Knowledge Management Is an Extension to HRM?

The spectrum of innovation has immensely expanded the ambit of HRM capabilities. The incidence of continuous innovation in every filed of HRM like selection, performance management, training & development etc. has made phenomenal changes to bringforth new directions and domain of thought processes as outcomes that are assimilated in the organizational ecosystem and practiced by the successful mediations and interventions of KM by means of development, dissemination and application of knowledge [8]. Collaborative and holistic practices of KM-induced HRM essentially enhance the uniqueness of organizational competency preferably the knowledge protocol, which positively signifies the association with the extent of innovations not the other way around, i.e. knowledge HRM (KHRM) has no impact on innovation excepting to mediate between collaborative HRM as transformational change agent [5].

1.4 Knowledge Management in the 4IR

There is symbiotic relationship between knowledge management and the progression of 4IR. The fourth industrial revolution has been continuously expanding the knowledge sharing platform so that it can move forward endlessly in consonance with the rapid research and development outcomes. From the beginning of twenty-first century, the world of technological research largely dominated by splendours of electronic gadgets, IoT, machine learning, block chain technology which facilitates to generate record process and interpret the large volume of data which is popularly known as big data analytics which primarily solve the problem by means of various modes of descriptive, predictive and prescriptive data analysis. All these development vectors in the technological framework and high yield application mechanism to solve complex problems have essentially deserved the transformative knowledge management initiatives in the organizational set-up.

2 Objectives of the Study

1. To propose a logical model to understand the interrelationship between progression of industrial revolutions ab initio and individual firms' aspirations for bridging knowledge gaps.
2. To develop a conceptual framework for understanding interrelations and interactions among industrial progression (4IR), knowledge management and transformational HRM practices using HRM competency model.
3. To devise the knowledge-dominated KASH protocol in HR interventions in congruence with the progression of industrial revolution.

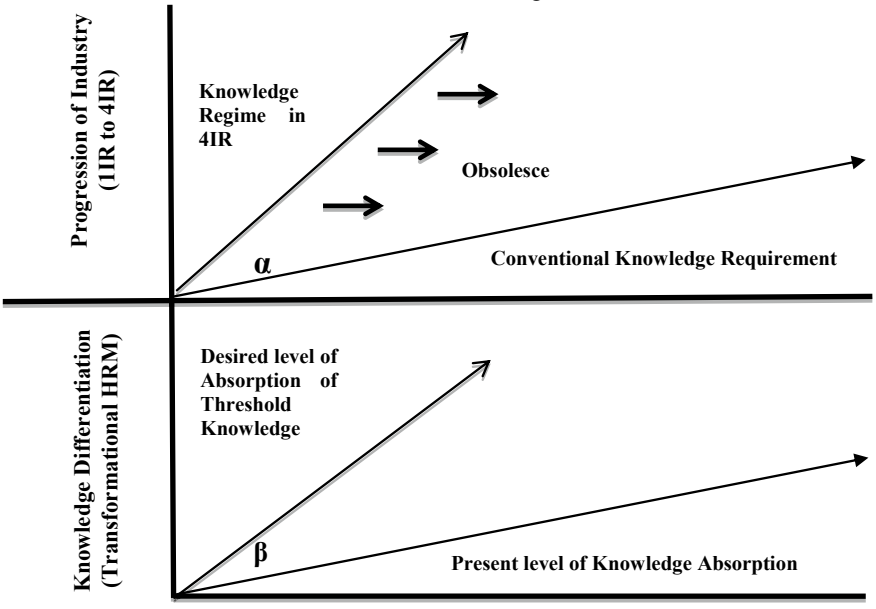
3 Research Methodology

This is an exploratory study through which it is attempted to understand the premises and fitness of knowledge management in the emerging 4IR ecosystem. The paper has been designed referring various research papers, reports and suitable application of strategic evaluative protocols widely practised in the academia and the research world.

4 Analysis and Interpretation

4.1 Analysis & Interpretation—I

According to Watson [12] knowledge is regarded as an ability to utilize information in order to add value and influence the decision-making process. It is imperative that the organization should adapt the terminal level of knowledge in a useable form so that there should not be much deviation of standards between industry and firms in terms of creation, transfer and utilization of knowledge [10].



$\alpha \propto \beta$

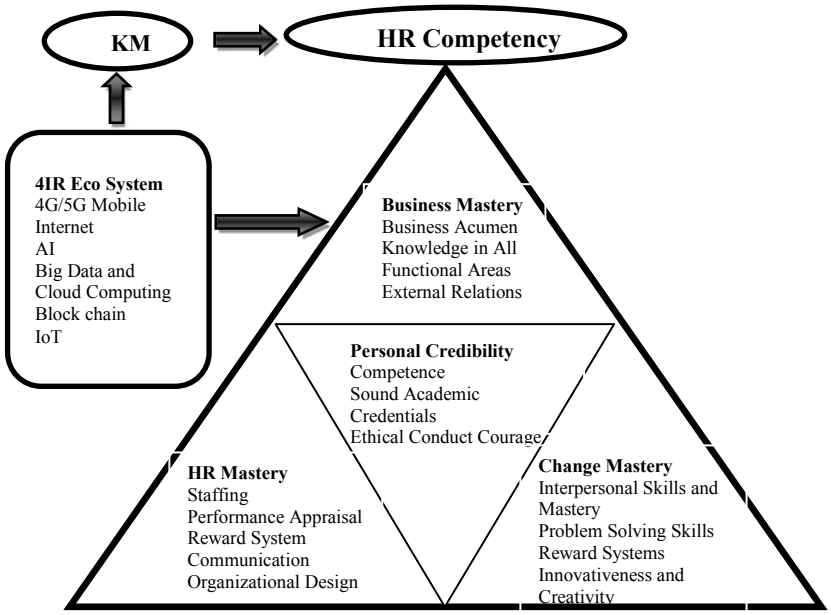
Model developed by the Authors

The journey of industrial revolution has been largely manifested by the voracity of knowledge which has emerged thorough the continuous process of innovation. In the comparative two-dimensional matrix, the angle (α) between conventional knowledge requirement and knowledge regime in 4IR increases with the fact that

'knowledge regime in 4IR' would tend to incline to Y-axis with the passage of time. Similarly, the angle (β) between the 'present level of knowledge absorption' and the 'desired level of absorption of threshold knowledge' must escalate in proportionate with the time spend and experience gathered. For every organization to survive in the dynamic environment and technological development, the angle α and β must be proportional and highly correlated in order to signify that the organization would remain competitive as it enjoys competency in the incremental knowledge-dominated industrial revolution. If the organization fails to achieve this synergy, it would literary cease to exist. The upsurge of 'knowledge regime in 4IR' tends to incline towards *Y*-axis which makes the curve stiffer enhancing the value of angle α. As a result of that, it forces to dissociate the previous knowledge set to become obsolete as depicted in the model.

4.2 Analysis & Interpretation—II

The progression of knowledge intends to augment the process of industrial revolution (IR). The set of ongoing innovations essentially land up with a new age and phase of IR; thus, human society moves forward from the primitive era of 1IR to the most advanced knowledge-driven industrial revolution popularly known as Industry 4.0. The industrial environment essentially influences the appropriate inducement of knowledge that can generate higher order of competency uniqueness for the firm. In order to explore these opportunities, the firm needs to invest on high-end resources as well as procurement of superior human resources that can augment and transform the change management initiative at possible encounter. The new era of knowledge management imbibes the HR policies to encourage and promote the best talents to acquire so that the culture of learning organization can perpetuate with higher acceleration as in tune with the expectations of the relevant industry.

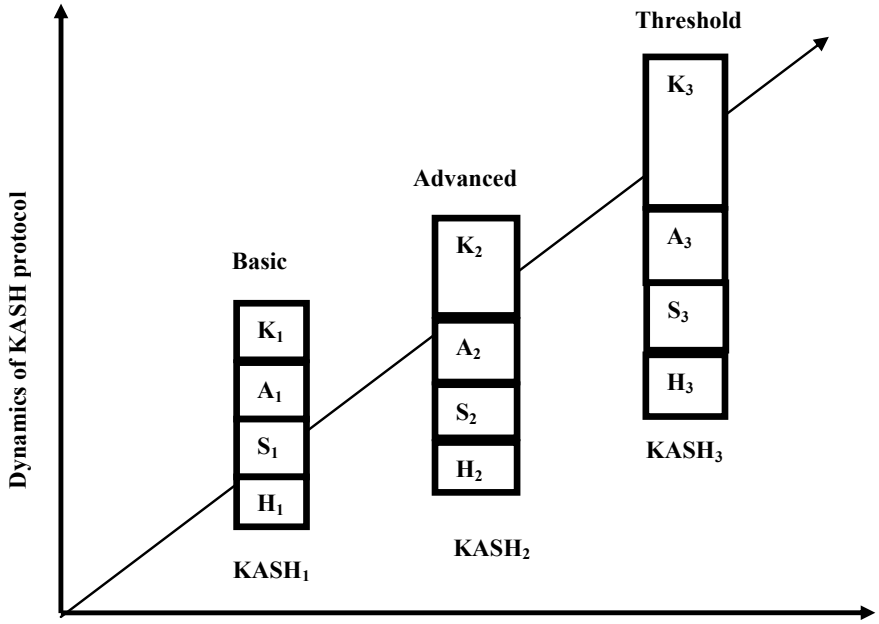


Model developed by the Authors in corporation HR Competency Model adapted from Human Resource management by Christopher Maybe, et. al., Blackwell Business, p.31

The model has been developed to project how the industry environmental factors reign enforces the firm to prioritize knowledge management which can be trickled down even at the bottom of the pyramid in the organizational hierarchy. This holistic development vector has to be inundated by the dynamic HRM practices as depicted above.

4.3 Analysis & Interpretation—III

The basic function of HRM revolves on its effective strategies human resource planning, performance management and human resource development which also interacts and correlates each other. One of the important approaches to address the HRM functions may be the successful manifestations of Knowledge, Attitude, Skills, Habits (KASH) protocol.



Model developed by the Authors

KASH denotes the assortment of four components: Knowledge (K), Attitude (A), Skill (S) and Habits (H) which are primarily required for a certain position of an organization in a mutually exclusive manner. KASH differential matrix examines the differentials of each component with respect to the deviations from the actual level of performance from its desired/expectancy module.

The firm always looks at the KASH differential matrix as illustrated below.

KASH components	Desired KASH set	Actual KASH set	KASH differentials (D~A)
Knowledge (K)	K_D	K_A	K_D~K_A
Attitude (A)	A_D	A_A	A_D~A_A
Skills (S)	S_D	S_A	S_D~S_A
Habits (H)	H_D	H_A	H_D~H_A

~ Sign of difference

If ($K_D < K_A$) or ($K_D = K_A$), i.e. the knowledge set desired is either lesser or equal to the knowledge possessed by the existing professional, no training need is identified / required. In general cases, K_D happens to be greater than K_A that means, the desired knowledge is greater than the actual knowledge possessed by the concerned employee that symbolizes the specific requirement of knowledge, i.e. identification of training need on specific knowledge domain. The firm would attempt to minimize the $[K_D - K_A]$ by means of appropriate HR interventions. Similarly, other **KASH** components can also be described. The most feasible 'K', 'A', 'S', 'H' combinations are generally encouraged for achieving desired HR objectives. With the growing influx

of knowledge management, the appropriate '**KASH differential matrix**' needs to be formulated, giving increasing weightage on knowledge components as per the dynamic demands of 4IR and so on.

5 Conclusion

Experiential learning and Research & development generate new idea product process for the welfare of mankind. The benefits of such illustrious development can reach to the people if it is implemented effectively and efficiently. It is a turn for the industry in general and the firm in particular to adapt such changes by augmenting advanced knowledge management protocol. The transformation process needs appropriate HR interventions that can only ensure this transition in an accelerated change management initiative. This paper has presented conceptual framework to understand the interrelations and interventions of KM and transformational HRM through along the progression of industrial revolutions more precisely 4IR ecosystem.

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Preface

The 4th International Conference on Research in Intelligent and Computing in Engineering, popularly known as RICE 2019, was held on August 08–09, 2019 in Hanoi University of Industry (HaUI), Hanoi, Vietnam.

The Fourth edition of RICE 2019, organized by the Electronic Engineering Faculty of the HaUI, provides an international forum which brings together the researchers as well as the industry practitioners, who are actively involved in the research in fields of intelligent computing, data science, or any other emerging trends related to the theme covered by this conference. RICE 2019 provided an opportunity to account state-of-the-art works, to exchange ideas with other researchers, and to gather knowledge on advancements in informatics and intelligent systems, technologies, and applications.

This conference has technical paper sessions, invited talks, and panels organized around the relevant theme. RICE 2019 was the event where the author had the opportunity to meet some leading researchers, to learn about some innovative research ideas and developments around the world, and to become familiar with emerging trends in Science and Technology.

RICE 2019 received a huge response in terms of submission of papers across the countries. RICE 2019 received papers from various countries outside Vietnam such as India, China, Russia, Australia, New Zealand, and many more. The Organizing Committee of RICE 2019 constituted a strong international program committee for reviewing papers. A double-blind review process has been adopted. The decision system adopted by EasyChair has been employed and 118 papers have been selected after a thorough double-blind review process. The proceedings of the conference will be published as one volume in Advances in Intelligent Systems and Computing, Springer, indexed by ISI Proceedings, EI-Compendex, DBLP, SCOPUS, Google Scholar, and Springerlink.

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Hyderabad, India — Vijender Kumar Solanki
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Contents

Promoting Green Products Through E-Governance Ecosystem: An Exploratory Study

Arindam Chakrabarty, Mudang Tagiya and Shyamalee Sinha

Abstract Green product is the future of global sustainability. The e-governance has been emerged as a form of effective and efficient strategy of the state to optimize its resources and delivery mechanism. The green product needs serious attention, encouragement, investment, and effective promotional strategies so that it gathers the desired momentum in the market. This paper has attempted to understand the basic concept of green products and its various illustrations across diversified product segments. The paper has proposed a conceptual model which is simple but effective to encourage the consumers by appropriately exercising reward-incentive mechanism. This research paper is exploratory in nature, which has been developed using various secondary information and research outcomes.

Keywords Green products · Sustainability · Green technology · E-governance · Ecosystem

1 Introduction

1.1 Green Product and Commitment Toward Environment

There are products having the feature of less impact on the environment or are less detrimental to human health than traditional equivalents. Such products fall under the category of green products. These may be developed or partly developed from recycled components, manufactured in a more energy-conservative way, supplied to the market with less packaging, or manufactured from local materials to reduce the need for transportation and also reduce carbon footprints. In today's world, the

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planet needs to be protected. Human greed and selfish ambition has exploited the resources and put the planet in a critical predicament. By using and promoting the green products, one may contribute to the safety and preservation of the resources provided from the planet, such as metals, plastics, and even water. Today, more number of people needs to be aware about green products and its application so that it would benefit all living beings in the planet earth. The term development has been perhaps wrongly or narrowly manifested within the locus of massive infrastructure, construction, and building of engineering structures to jump from natural green to jungles of concrete. The north-eastern states are still alive with its flora and fauna. If the adoption of green products has not been incorporated by upcoming generations, the flood of indiscriminate and irresponsible consumerism would sweep the core values of sustainability for the region and for the entire nation [1].

1.2 Emerging Green Management Practices

1.2.1 Green Marketing

Green marketing incorporates a broad range of activities, including product modification, changes to the production process, packaging changes, as well as modifying advertising. Yet defining green marketing is not a simple task. Indeed, the terminology used in this area has varied; it includes: green marketing, environmental marketing, and ecological marketing. While green marketing came into prominence in the late 1980s and early 1990s, it was first discussed much earlier. The American Marketing Association (AMA) held the first workshop on "Ecological Marketing" in 1975 [2]. Green or environmental marketing consists of all activities designed to generate and facilitate any exchanges intended to satisfy human needs or wants such that the satisfaction of these needs and wants occurs, with minimal detrimental impact on the natural environment [3].

1.2.2 Green HRM

Nowadays, green HRM has become a significant thrust area for management which can have an enormous impact on people issues in an organization.

It is the application of HRM policies in the way to encourage sustainable use of resources in an organization by increasing awareness and commitments among the employees toward the issues of sustainability to protect and preserve natural resources. It consists of two important elements, that is, environment-friendly HRM practices and the protection of knowledge capital. Green HRM consists of process and practices, like acquisition, induction, training, performance management, and reward system, which have a bearing on the whole carbon footprint of an organization. Green practices under green HRM that are followed by the company are power saving, internal environment and energy audit, eco-friendly or green surveys, going paperless

by using software and apps and so on, recycle waste, water saving, alternative energy sources and so on.

1.2.3 Green Finance

Green finance refers to financial investments flowing into sustainable development projects and initiatives, environmental products, and policies that encourage the development of a more sustainable economy. Green finance includes climate finance but is not limited to it. It also refers to a wider range of other environmental objectives, for example industrial pollution control, water sanitation, or biodiversity protection. Mitigation and adaptation finance is specifically related to climate change related activities: mitigation financial flows refer to investments in projects and programs that contribute to reducing or avoiding greenhouse gas emissions (GHGs) whereas adaptation financial flows refer to investments that contribute to reducing the vulnerability of goods and persons to the effects of climate change [4].

1.2.4 Green Technology, Green Manufacturing, and Green Services

Green technology is considered as environment-friendly based on its production process or supply chain. It also may refer to a means of energy production that is less harmful to the environment than more traditional ways of generating energy, such as burning fossil fuels. This technology is considered as young market comparatively, but investor's interest runs very high in response to global warming fears and the increasing scarcity of many natural resources (*Investopedia*). It aims to conserve nature and mitigate the impact of human activities. This technology provides the benefits not only to nature but also for a clean and greener human lifestyle. This technology ensures that the earth remains well for all generations and exist. On the other hand, the "green" manufacturing is known for the renewal of production processes and the establishment of environment-friendly operations within the manufacturing field. In the process the workers use minimal natural resources, reduce pollution and waste, recycle and reuse materials, and moderate emissions in their processes.

2 Theoretical Background

There was a time where many practicing managers regarded a preoccupation with green management almost exclusively as a threat. Nowadays, it is more widely accepted that green management can be profitable [5–7]. Green management can act as a vital role in the optimization of production processes and new-product development, not only in pollution-sensitive industries, such as petrochemicals and electric power and manufacturing, but also in high-tech industries [8]. The need for

green management springs from a variety of sources, including societal mandates incorporated into laws, treaties, and regulations [9].

Since green management is a type of public good, whose full value a firm cannot entirely appropriate [10], government's role in the acquisition of green capabilities is obviously important [11]. Management or managers should pre-define green goals, targets, and responsibilities for their strategic business unit, and corporates should assess number of green incidents, use of environment responsibility, and successful communication of environmental policy within their scope of their operations for improving the performance [12, 13].

3 Objectives of the Study

I. To study the concept of green product and its representation across various product segment.
II. To formulate comprehensive model and flowchart to increase and optimize green movement in India through efficient e-governance.

4 Research Methodology

This paper is designed on the basis of various reports, articles, research papers, and information collected from varied secondary sources. The conceptual model has been proposed in order to motivate the users toward green products by establishing real-time network with the market players. The e-governance framework may retrieve adequate information about the green product and its purchase indents so that it could establish a structured reward-incentive mechanism for promoting green marketing.

5 Analysis

5.1 Analysis—I

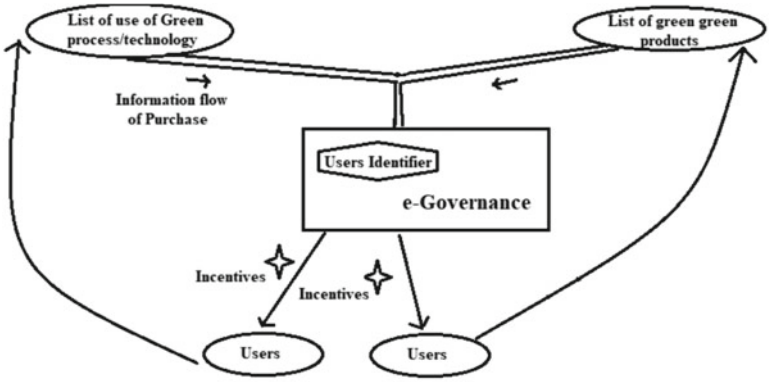
The wave of sustainable development has drawn the attention of the manufacturers, service providers, users, policy makers, and so on across the globe. It has been trickle down from the developed economies to the developing nations of the world. The affinity of the people of India has been increasing to the extent that it has found that the propensity of using green products has been significantly observed among the indigenous community of Arunachal Pradesh, the least population density state in India [1]. The study conducted by Chakrabarty and Tagiya [1] has emphasized that the attitude of the consumer toward environment and green products has combined

effect on favorable purchase intention behavior. However, price sensitivity, quality enhancement, brand familiarity, ease of access, and convenient to use are the decisive factors that influence the attitude of consumer toward green product. The availability, ease of access, and awareness of green product predominantly encourage the buyers for purchasing or availing green product or green technology. The green products are gaining popularity day-by-day and it became available in various sectors, for example, FMCG, consumer durability, health care, white goods, packaging material, and transportation. The indicative list of green products is illustrated below:

FMCG Sector: Biodegradable detergents, soaps, green tea, eco-friendly disinfectants, all types of papers (writing papers, tissues, toilet).
Consumer Durable Segment: Recyclable batteries, LED light bulbs and tubes, solar panels, clay-based cutlery, and crockery.
Health Care Sector: Biodegradable fittings and fixtures, cotton-based consumables for dressing or bandit materials, cotton bed sheet, eco-friendly disinfectants, biodegradable gloves.
White Goods Segment: Water heater tank (electric), dish washer, high-efficiency washing machine and clothes dryer, induction top cooker, energy star refrigerators, vacuum cleaner, dual-blade twin window fan.
Packaging Industry: Edible package material, paper bags, tetra-pack package.
Transportation sector: Bio fuel, low-carbon emission gas (CNG), recyclable tires.

5.2 Analysis—II

The popularity and penetration of green product may essentially be enhanced by the collective efforts of all the stake holders, including the dominant role of the government. The strategic and interactive roles among the stake holders are the prerequisite for enabling the green products in the demand baskets of its users. The strong network needs to be established that would yield desired result for effective promotion strategy of green products. A conceptual model has been proposed where the e-governance can facilitate to promote green consumerism.



Positive Reinforcement Model for Green Product through e-Governance

5.3 Modus Operandi of Proposed Model

Step 1*: The Government should identify the lists of green products, green technology, and green processes. Appropriate awareness campaign may be initiated to create customer pool for this segment.*
Step 2*: The market players may be identified and are established with the real-time network through which any transaction made at their end may send the overview of purchased details.*
Step 3*: Based on the purchase details, the customer profile would be identified and tracked. The incentive package or any form of subsidy may be extended to the identified customer through electronic transfer in the form of "Direct Benefit Transfer" (DBT).*
Step 4*: The real-time reward-incentive mechanism would reinforce and promote the green product among the target segments.*

6 Conclusion

In the dynamics of fourth industrial revolution, to apply threshold level of technology emerged, particularly in the domain of IoT ecosystem. This is high time to create appropriate interface and network between public–private interactions through new generation devices. The e-governance is quite popular and useful in augmenting the efficient delivery system across the world even in India. The success of smart card in Andhra Pradesh is the testimony of India's success story where the system minimizes its leakage [14]. The paper has showcased how the appropriate reward-incentive mechanism can be offered to the green product users using augmented electronic governance. This model may be implemented that would essentially increase green

consumerism in the market, which in turn would fulfill the commitment of sustainable development as expressed in Brundtland Commission 1987.

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Advances in Intelligent Systems and Computing 1125

Vijender Kumar Solanki
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Prasant Kumar Pattnaik *Editors*

Intelligent Computing in Engineering

Select Proceedings of RICE 2019

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Preface

The 4th International Conference on Research in Intelligent and Computing in Engineering, popularly known as RICE 2019, was held on August 08–09, 2019 in Hanoi University of Industry (HaUI), Hanoi, Vietnam.

The Fourth edition of RICE 2019, organized by the Electronic Engineering Faculty of the HaUI, provides an international forum which brings together the researchers as well as the industry practitioners, who are actively involved in the research in fields of intelligent computing, data science, or any other emerging trends related to the theme covered by this conference. RICE 2019 provided an opportunity to account state-of-the-art works, to exchange ideas with other researchers, and to gather knowledge on advancements in informatics and intelligent systems, technologies, and applications.

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Contents

Intervention of Smart Ecosystem in Indian Higher Education System: Inclusiveness, Quality and Accountability

Arindam Chakrabarty, Mudang Tagiya and Shyamalee Sinha

Abstract In the knowledge age, the human society largely depends on both inclusive growth and superior quality of higher education system. The world is transforming very fast and it tends to celebrate the fourth industrial revolution that extends from the information processing and automation to the extent of replication of human intelligence. The emerging protocol of artificial intelligence, RFID, cloud computing, block chain and machine learning are the gamut of resources which essentially would embody the teaching–learning process more effective and result-oriented. In India, the use of e-resources like MOOC, e-learning, Swyam have been experimented and they enjoy popularity and success among the users. However, the higher education system of the country is severely compromised by regular flow of information and databases. It is affecting the quality of teaching–learning process and research. It is high time to have a centralized database reservoir which would contribute to every learning organization, irrespective of government, private or NGO. The database would be collected and preserved by a national e-resource portal which could be accessed by any individual or institution with or without any processing fees; otherwise the direction and continuum of academia and research would have to be severely affected. The present study has attempted to showcase how the various e-resources are integrated into Indian education system. The paper would also approach and present a prototype model on how a comprehensive e-resource portal can be developed and optimized to ensure collection, preservation and access of data set.

Keywords Higher education · Smart ecosystem · e-resource portal · Inclusive growth · Accountability

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1 Introduction

1.1 India and Higher Education

During the ancient era, the scenario of Indian education consists of '*Gurukul System*' which mainly concentrated on education to developed knowledge. The *Guru* (referred to the teacher) will train their '*Sishya*' (referred to the students) through yoga, meditations and various standards. The early education system in India eventually got unnoticed due to series of invasions and dispute in the country. In the beginning of modern age, the Islamic influences improved the outdated education centers and brought in the broad domains, like geography, administration, law, arabic, mathematics and so on, into India. Colonial rulers who ruled India brought a significant transformation in the higher education system. It was the British who set up the formal system of higher education dedicated to the disciplines, like *languages, literature, history* and *philosophy*. In India, the higher education system started to grow rapidly after independence. The study shows that during the year 1980, there were 132 universities and 4738 colleges, enrolling around 5% of the eligible age group in higher education. The total number of educational institutions in India was four times higher than the overall number of institutions present in both United States as well as Europe. Today, India is advancing toward modernization, technology, communication, education and economic growth. It is giving a tough competition to other developed nations in the field of high-tech industries, such as agriculture, medical, information technology, energy and power, and biotechnology to drive the nation to opulence. In the present day, Indian higher education system holds an important place in the global education industry. India has one of the largest networks of higher education institutions in the world and is the third largest in the world. The UGC—an apex body established in the year 1949—essentially deals with the setting up and maintenance of standards in higher education throughout the nation on a uniform basis. The Central Government has been playing a key role in providing overall policy directions and thus acts as a vital link between the policy-making bodies of the government and institutions of higher education. With the introduction of various policies on higher education and subsequent programs undertaken to operationalize the policy has significantly impacted the growth and development of higher education in India. The important landmarks in the evolution of policy in higher education are as under:

Evaluation of Higher Education Policy in India	Year
University Education Commission	1948–49
Education Commission	1964–66
National Policy on Education	1968
Policy on Education (Draft)	1978

(continued)

(continued)

Evaluation of Higher Education Policy in India	Year
National Commission on Teachers-II	1984
Challenge of Education: A Policy Perspective	1985
National Policy on Education	1986
National Policy on Education: A Program of Action	1986
National Policy on Education: A Program of Action	1992

Source IGNOU study material for PGDHE (MES-101, Block-2, Unit-6, pp. 23

1.2 Emphasis on ICT in the Higher Education Policy

In the year 1984–1985, the need of '*Information and Communication Technology*' (ICT) in education sector has been recognized in India. It was realized when the program called *Computer Literacy and Studies in Schools* (CLASS) was introduced on experimental basis, and the project was later on adopted as a centrally sponsored scheme during the seventh Five-Year Plan (1993–1998). Eventually, the scheme was extended in eighth plan to provide financial grants to institutions covered earlier and to include new government-aided secondary and senior secondary schools. The financial assistance included annual maintenance grant and purchasing equipments for new school. During this period 2598 schools were covered. In the mid-1998, the information technology and software development (IT taskforce) came into the picture for the purpose of recommendations on introduction of IT in education sector including school. The report recommended the provision of computer system to all educational institutions up to higher secondary schools by appropriate investments (about 2–3%) of total budget during the next five years. During the year 2001–2002, a revised class scheme was introduced by making the provision of Rs. 845 million on recommendation. The applications of ICT for quality improvement were also included in Government of India flagship program on education, viz., Sarva Shiksha Abhiyaan (SSA).

2 Literature Review

[1] ICT in Indian University and colleges shows the revolution of higher education in the nation, in terms of access, equity and quality with the application of ICT in education. The various prospects and challenges posed by amalgamation of ICTs in various aspects of higher education in the present scenario are discussed and factors regarding future development in ICT in education sector are also highlighted.

Information and communication technology (ICT) plays a major role in supporting powerful, efficient management and administration in education sector. It is stated that ICT may use right from student management to various resource management in an education institution [2].

The e-learning and pedagogical innovation framework at Leicester provided a proper stage for the number of formal and informal discussions required to develop an e-learning strategy for the university [3].

ICT evolves as an instrument toward advanced knowledge. As learning tool, that is, ICT, it enhances the human intellectuals and capabilities in solving problems, helping and benefiting the students in gaining and increasing knowledge, and promoting the faculties, teachers, trainers and administrators in improving teaching and learning. This technology has also incorporated the knowledge and skills required to effectively use ICT as a tool [4].

Even though the application of ICT is not the answer for all the challenges faced by higher education systems in the region, it does leverage and extend conventional teaching and learning activities, and has the potential to positively influence on learning [5].

The application of information and communication technology (ICT) in higher education system has resulted in shifting from teacher-centered delivery and transmissive learning to student-centered learning. ICT acts as a channel of information, and intellectual tools have been supporting and serving the students to be mature enough and become responsible toward learning [6].

3 Objectives of the Study

I. To explore the application of smart eco-system in Indian higher education system.
II. To formulate integrated and smart strategy framework for sharing information through the man–machine interfaces across the country.

4 Research Methodologies

This study conceptual in nature is based on information collected from secondary sources like reports, journals and so on. The paper attempts to understand the present scenario of smart eco-system used in higher education system in India and attempts to

formulate a schematic model where the advance smart eco-system would be deployed the available resources to enhance quality of the higher education.

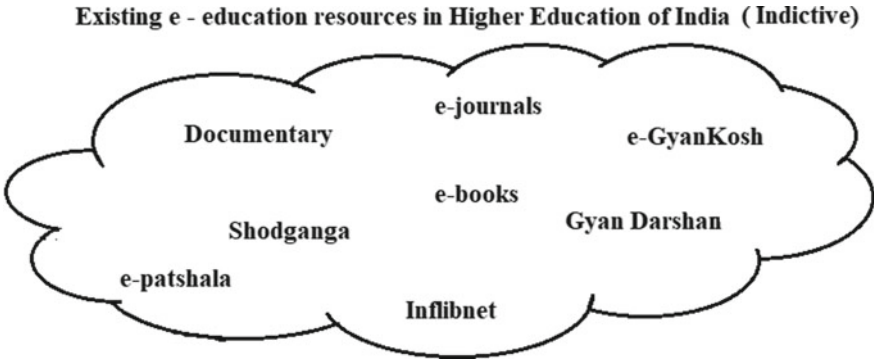
5 Analysis and Interpretation

5.1 Analysis—I

Various e-resources on education	
E-resources from MHRD supported programs	Other learning resources
NPTEL (https://nptel.ac.in/)	Digital Teaching and Learning Resources for PwDs (http://www.ayjnihh.nic.in/Digital_teach_resources.asp)
Virtual Labs (http://www.vlab.co.in/)	LILA Hindi Pravah
Spoken Tutorial (https://spoken-tutorial.org/)	Physics—Mysterious Magnetism (http://www.youtube.com/watch?v=wKdqCqTzSnI&list=PLdm-2_AHi21QoOEbiVEMty8vy6yS3UWF3&index=4)
The Consortium for Educational Communication (http://cec.nic.in/Pages/Home.aspx)	Astronomy—Eclipse (http://www.youtube.com/watch?v=Q1yq2LpQ-Qc&list=PLdm-2_AHi21QoOEbiVEMty8vy6yS3UWF3&index=28)
e-Yantra (https://www.e-yantra.org/)	Astronomy—Day and Night
e-ShodhSindhu (www.inflibnet.ac.in/ess/)	Khan Academy
FOSSEE (Free and Open Software in Education) (https://fossee.in/)	CS Unplugged
	Coursera
	Udemy (http://www.youtube.com/watch?v=Q1yq2LpQ-Qc&list=PLdm-2_AHi21QoOEbiVEMty8vy6yS3UWF3&index=28)
	MITOCW (https://www.edx.org/)
	LEARNING SPACE:THE OPEN UNIVERSITY (https://www.open.edu/openlearn/)
	Vidya Online (http://www.vidyaonline.net/index.php)

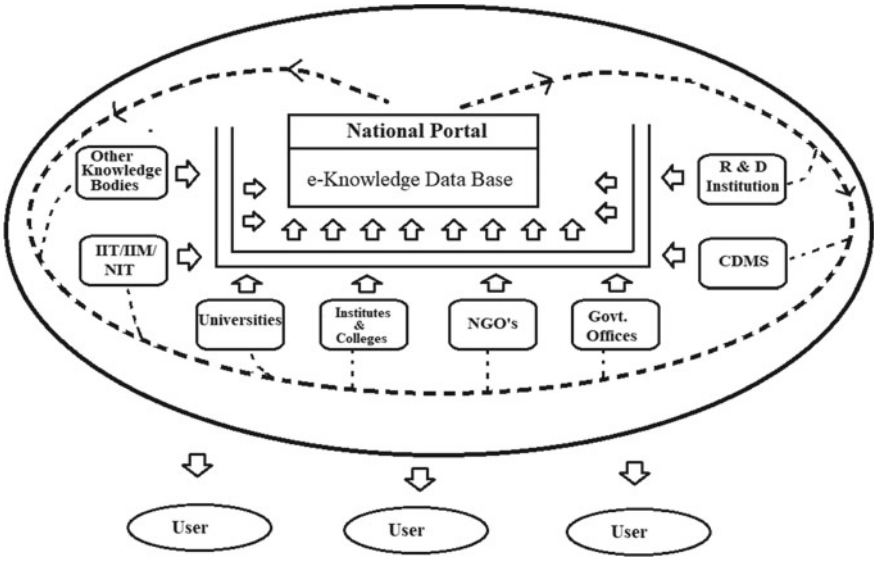
Source http://vikaspedia.in

India has been using e-education resources since early twenty-first century. The application of ICT has been pioneered in a few open and distance learning program and online courses offered by both govt. and private enterprises with the pace of phenomenal growth in satellite technology, access to the internet and even high-configuration mobile usage. The importance of e-resources has been well thought and adopted. The indicative list of popular e-education resources in India is mentioned below:



5.2 Analysis—II

The growth of higher education system largely depends on creation of new knowledge, development of contents, smart dissemination process and application-based research. In India, various sectors and agencies are working in their respective domains but observations, outcome and experiences are not adequately shared among all its partner, stakeholders and users. These create massive hindrance for the learners, researchers and the implementing agencies to achieve success in their respective intellectual pursuits. The lack of data support or exchange leads the society toward policy paralysis. India is in the alarming position where all the knowledge-generating, policy-making and research organization need to interact freely with their databases, sharing of experiences and critical observations. The paper has coined this urgency and has attempted to device an integrated e-resource portal which would perform the task of continuous data collection, preservation, its uninterrupted flow of processing across the entire stakeholders.



Modus Operandi of the Proposed Model

Step—1: Creation of a dedicated e-knowledge national portal/database. It can be created by appropriate enactment of law and with the consortium public–private partnership (PPP).
Step—II: All the knowledge bodies, institutes, private enterprises, non-government organization, govt.–pvt. establishments and so on compulsorily need to share their database, particularly R&D, process outcomes, achievements experiences or observations to the said national portal on regular interval. All the contributing institutional entities may be connected through appropriate network topology or modern gateway. It could also use the flowchart of electronic data interchange (EDI).
Step—III: All the data set/information would be collated, correlated and preserved so that the user's community across the nation can benefit from this system. However, access to the database may be free of cost or partially chargeable as the case may be depending on the rigor and cost implication of data procurement and its preservation. However, this national portal may exclude the information pertaining to security issues of the country, as well as the product/process secrecy, and others forms. In fact, the national portal would collate and preserve all the published information or documents in an integrated, coherent and synergic orientation.
Step—IV: The user may have to either subscribe with the portal or have to purchase the database if it is chargeable.

In the present context of Indian higher education system, it is difficult to access panel data or cross-sectional data, due to lack of integration of data across the stakeholders on a particular field of inquiry. The standard deviation and variation in data collected from different sources on a particular set of measurable attributes and entities sometimes appear to be very high. Few organizations that generate and

preserve database hardly share with the common users whether it is inaccessible, limitedly accessible or very costly for use. There are issues in generating particular set of database on regular intervals. The question of real-time data management is insignificantly exercised. In the corporate sector, the transparency and disclosure of information are limited and highly concentrated among few big players. All these catastrophic features of data generation, preservation and excess mechanism have largely affected the quality of higher education, teaching–learning and dissemination process. The research activities are severely compromised because of lack of availability or access to relevant data set. This paper has devised a comprehensive and nationwide data management ecosystem which would collate, collaborate and integrate all the relevant stakeholders for generating, preserving and sharing the platform for the users. The proposed national e-portal would ensure the authenticity, reliability of dataset and avoid data redundancy. This would ensure incremental access to such dynamic database platform which would trigger for achieving higher inclusive education. The projected model would perform the task of validating and integrating the database with higher precision and reliability which would ensure superior quality of knowledge exchange. As the system is reinforced by all the stakeholders of the country representing various segments of economy and intellectual acumen, the system is committed toward creating high-end value in the process of creating of knowledge and its dissemination, which shall reaffirm the spirit of accountability.

6 Conclusion

Information is the most decisive factor for success, particularly in the era of knowledge economy. Even in the ancient time the battle was fought among kings and the winning party did not conquer not only because of its marshal but of its strength in information search. This paper has shown the growing trend of using e-resources in the process of teaching–learning dissemination and research, particularly in the Indian context. However, there is lack of integrated approach to collate, preserve and share all the pertaining data sets among its users and stakeholders. This paper portraits a model solution by integrating all contributory institution with the national portal and in return the propagation of data flow from the portals to individual and institutional users with free access, limited access or paid access mechanism so that without compromising the sovereignty, security issues of the nation and without affecting the patent, copyright and commitments the country can foster high-end academic environment and experience the frontiers of research outcome.

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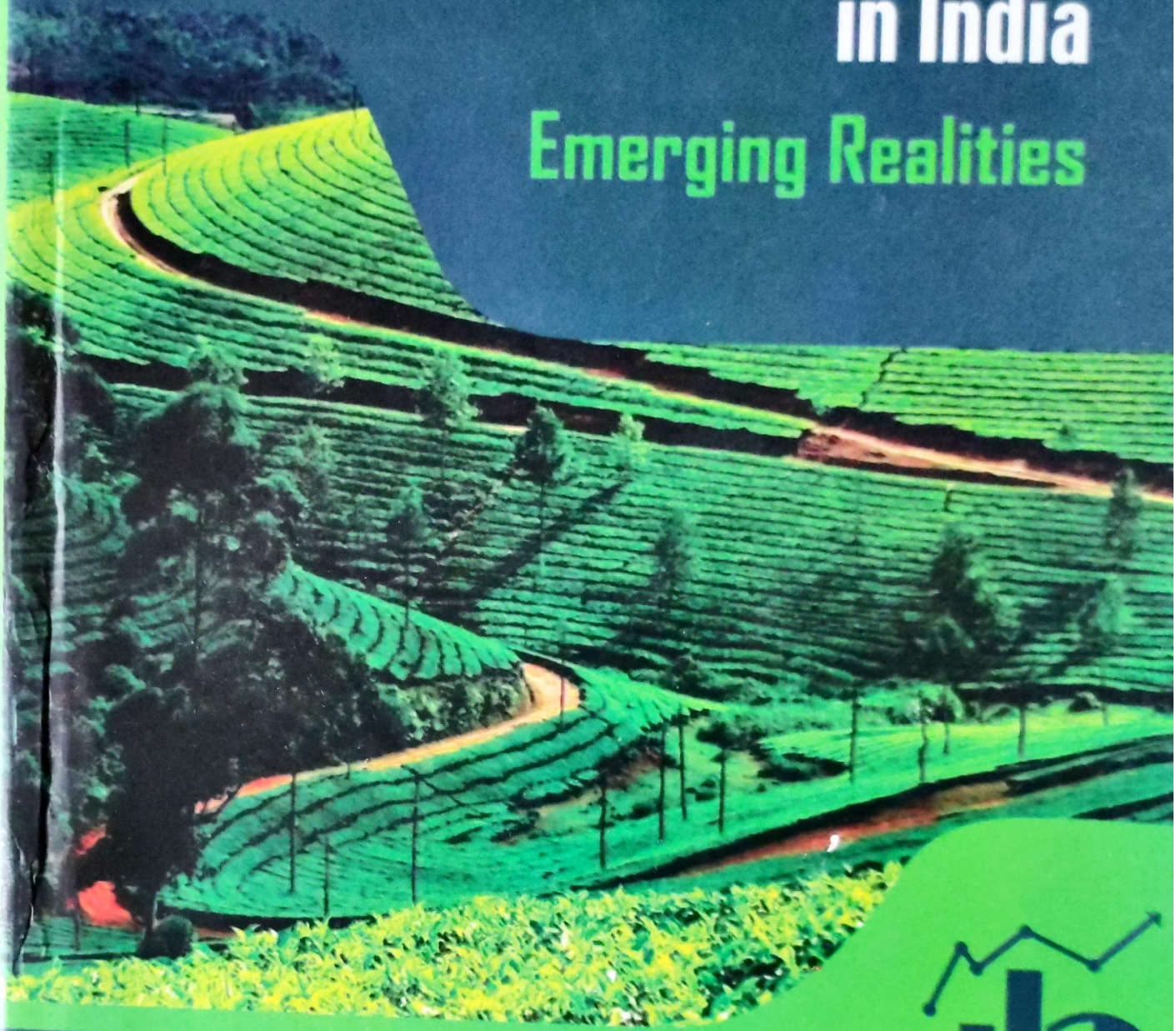

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Contents

17
State Finances of Arunachal Pradesh in the Post Reform Period

Anup Kumar Das and *Bhabesh Hazarika*

Introduction

The resource poor State of Arunachal Pradesh is highly dependent on central transfer of fund. It is having difficult hilly terrain and remoteness in the location. The State is backward in physical and social infrastructure due to high cost of production and resource constraints. Transportation is other major inherent challenge which has handicapped the state in a variety of ways. In this state, while the lack of own resources creates a budgetary hardship, the provisioning of public goods is very costly. For instance, Sarma *et al.* (2006) found that the per unit cost of provisioning merit goods like education and health in Arunachal Pradesh is two and half times more as compared to the plain areas (Nayak *et al.*, 2013). Considering the problems mentioned above, Arunachal Pradesh was accorded the 'Special Category' status along with other ten States by the National Development Council (NDC) as per there commendation of the Planning Commission. However, the State has not made any remarkable progress in its development by utilising the advantages of special category status. Recently, the transfer of fund under special category status has been stopped by the Union Government after coming to power in May 2014.

The economic reforms initiated in 1991could hardly make any contribution to Arunachal Pradesh and other special category States (Bhattacharjee, 2014). In fact, it constrained the States regarding access to soft central resources (Nayak *et al.*, 2013). The reform enhanced the growth of the country as a whole in general and the already developed

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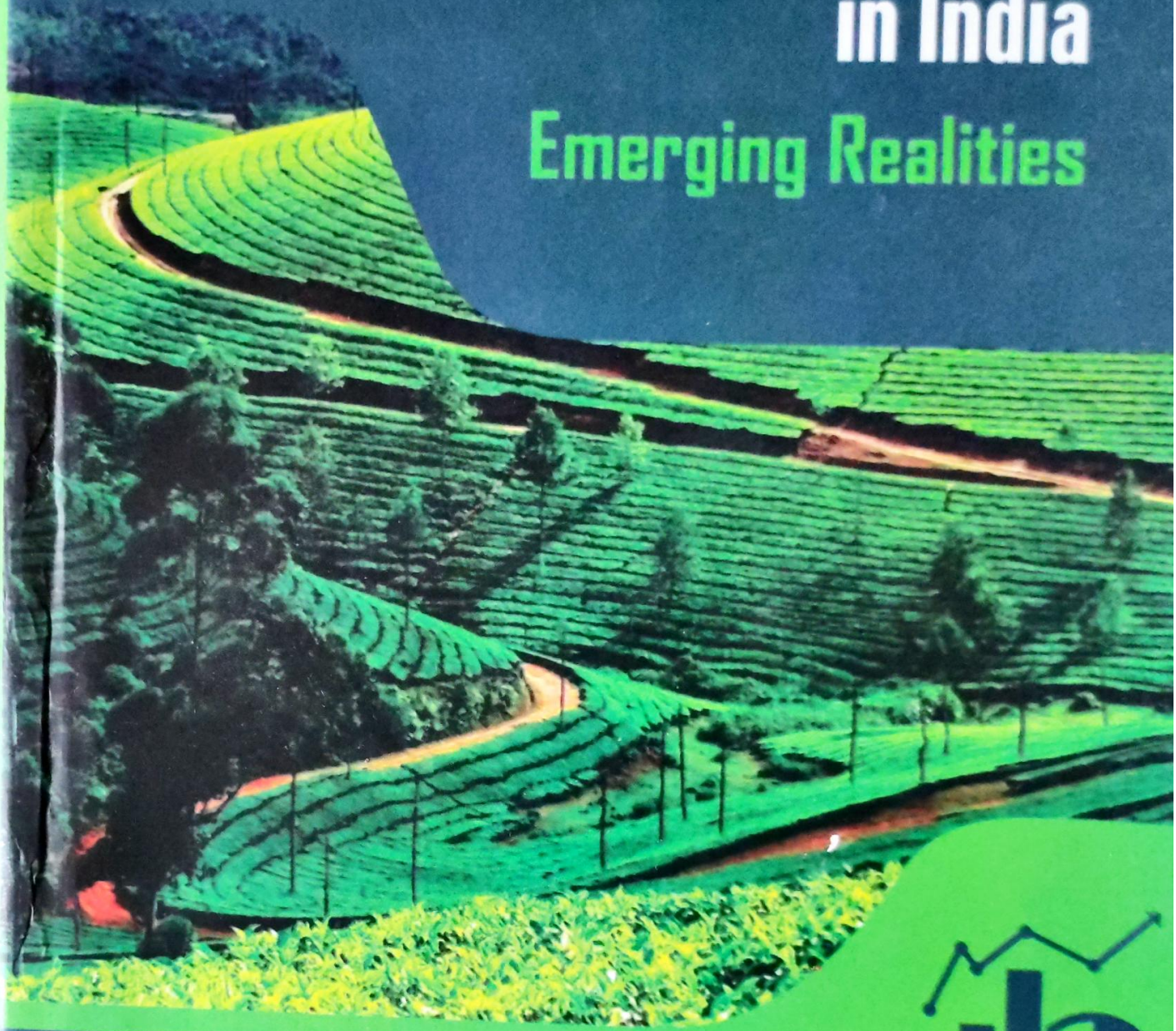

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20
Women's Work and Time Utilisation Pattern in Rural Arunachal Pradesh
A View from the Field

Dil Bahadur Gurung

Introduction

Women continue to do majority of the household work, whether employed or not, which is the most striking characteristics of household labour (Shelton and Daphne, 1996). In the traditional societies, domestic work is the main input for household production and consumption. Household economic activities consist of both market production and non-market production; and non-market production is meant for household consumption (Shimray, 2004). In rural areas, the basic nature of women work falls in the non-market activity. Women perform seasonal work, raising children, cattle work (milking, feeding and cleaning cow sheds), fetching water, fuel wood and fodder etc. "In poor agrarian economies with significant component of non-market activities the range of what constitutes housework is different from those of the advanced market economies. Boundaries of household work and economically gainful work are difficult to draw in such economies where non-market activities predominate" (Kalpagam, 1999).

Apart from domestic house work duties, women are involved in rural activities at varying level in different farming system across the globe. The most influential school of thought in explaining women's participation in agriculture is the one which views women's participation rates in agriculture by the nature of farming system (Boserup, 1970). There are the "female farming system" present in Africa, where 'hoe cultivation' is

RESEARCH TRENDS ON FISH & FISHERIES IN MOUNTAIN WATERS OF EASTERN HIMALAYAN REGION

This book contains a total of 25 unpublished research articles. In this edition, we have kept parity with each other's outcomes, concisely in a unique style to depict the trends of research in the mountain fishery sector. We have also appended a list of contributors at the end of the book. The strategies observed in fisheries and aquaculture developments in the mountain waters clearly reveal that the on-going dimensions are nothing but broad ecosystem-based approached where both subsistence and commercial expansion of the systems could be possible.

The research trend also directs that several fishery components, like ornamental fisheries, recreational fisheries, integrated fish farming, freshwater crab fishery, shellfish aquaculture, etc., exist. They may also be strengthened in mountain waters to improve the economic status of the mountain regions. Thus for exploiting huge mountain aqua-resources, Arunachal Pradesh targets the ecosystem-based approach of raising native mahseers, like *Tor tor, Tor putitora, Neolissochilus hexagonolepis*, and exotic species of trout in its mountain waters as a preliminary endevour.

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SECTION - III: SOCIO-CULTURAL ASPECTS OF HEALTH

SECTION - IV: HEALTH DETERMINING BEHAVIOR

SECTION - V: UNDERSTANDING AND CHANGING BEHAVIOR

16 Mental Health Stigma and Help Seeking Behavior Among Youth of Tribal Community of Arunachal Pradesh

Kakali Goswami and Leeyir Ete***

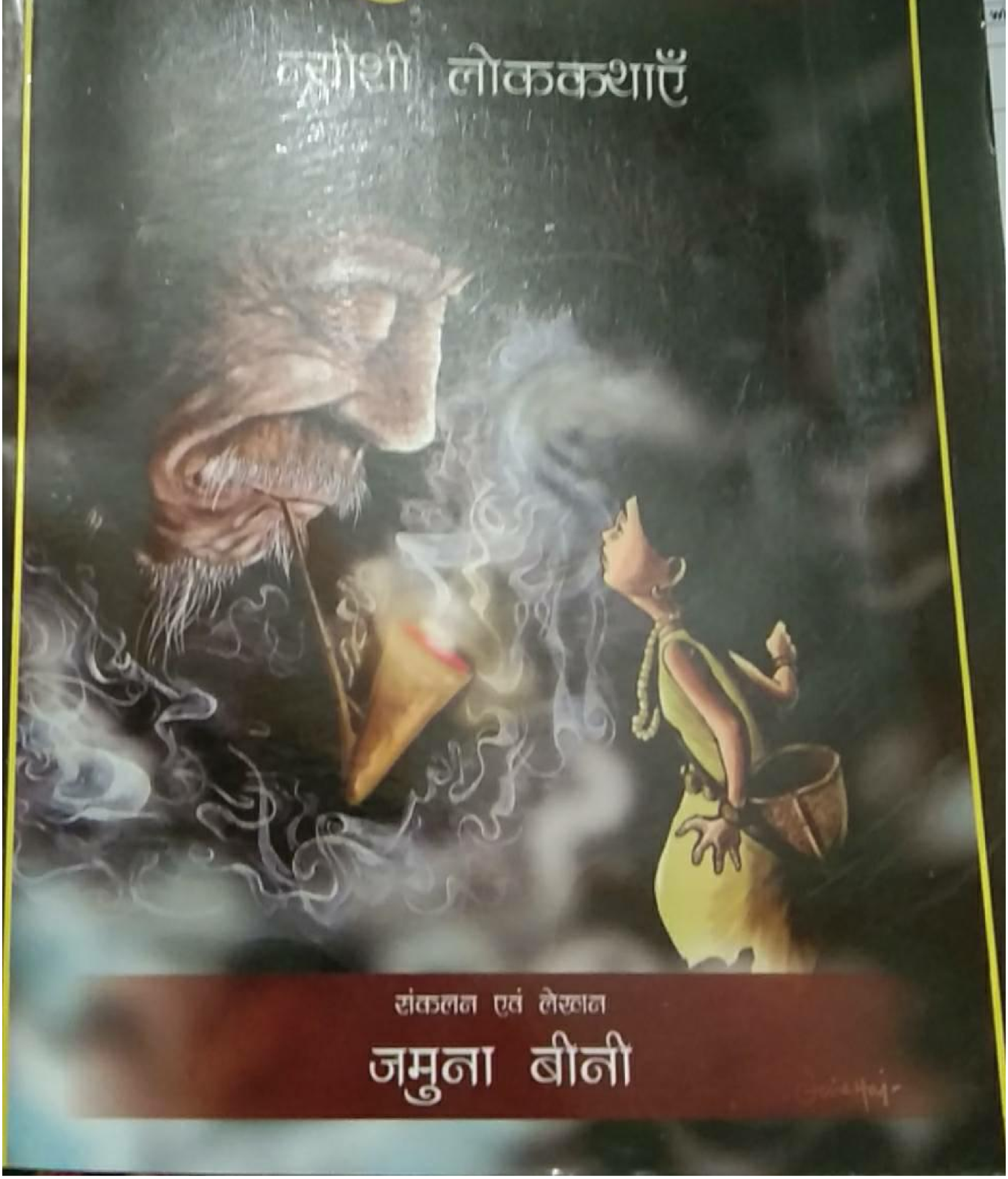
The present study was carried out to explore relationship between mental health stigmas and help seeking behavior. Because a person's attitude and belief regarding mental health can contribute to his/her help seeking behavior and self-care initiatives. The study was carried out among young people of various tribal community of Arunachal studying at university level to understand the level of awareness among people regarding mental health and help seeking behavior. A total sample of 50 was collected through survey. Two standardized questionnaire was distributed among the participants. The result of the study will interpret the percentage and belief and attitude of people toward mental health and also initiative towards taking help to deal with mental health and general health issues.

* Assistant Professor & Head I/C, Dept. of Psychology RGU, Itanagar, Arunachal Pradesh.

** Guest Assistant Professor Dept. of Psychology

उईमोक

नग्रोशी लोककथाएँ



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प्राक्कथन

जमुना बीनी की यह पुस्तक न केवल अरुणाचल अथवा पूर्वोत्तर के साहित्यिक परिदृश्य में वरन् हिंदी साहित्य के विस्तारित फलक पर भी महत्वपूर्ण सिद्ध होगी। इस बहुमूल्य रचनात्मक कृति का विचार उस समय पनपा जब जमुना बीनी 'जनजातीय साहित्य महोत्सव 2018' में सक्रियता से भागीदारी कर रही थी। पूर्वोत्तर के वाचिक साहित्य में अभिरुचि रखने वाले पाठक एवं विद्वानों को तो यह ज्ञात होगा ही कि पहली बार सन् 1958 में अंग्रेजी भाषा में वेरियर एल्विन की 'मिथस् ऑफ नेफा' पुस्तक प्रकाशित हुई थी। अरुणाचल प्रदेश की विभिन्न जनजातियों के मौखिक साहित्यिक परम्परा के गहन अध्ययन तथा मनन के लिए आज भी कई विद्वान उक्त पुस्तक का संदर्भ एवं उल्लेख देते हैं।

'उईमोक' अरुणाचल प्रदेश की न्यीशी जनजाति विशेष पर केंद्रित चित्रांकनों से सुसज्जित हिंदी में पहला और ऐतिहासिक प्रयास है। अरुणाचल के जनजातीय साहित्य की अपार संभावनाओं की खोज करते हुए इसे हिंदी के वृहद पाठकवर्ग के सम्मुख लाने के लिए नि:संदेह जमुना बीनी साधुवाद की पात्र है (उनकी निष्ठा, समर्पण एवं सुंदर प्रयास की जितनी भी भूरि-भूरि प्रशंसा की जाये कम है। हम सभी जानते है कि अकादमिक जगत में ईटानगर स्थित राजीव गाँधी विश्वविद्यालय के हिंदी विभाग की वह एक समर्पित टीचर है और सबसे मुख्य बात यह है कि वह हिंदी साहित्य में महत्वपूर्ण दखल रखने वाली पूर्वोत्तर की बहुचर्चित लेखिका भी है।

जेने हाई से मेरी प्रथम भेंट 2018 के अरुणाचल आर्ट एण्ड लिट्रेचर फेस्टिवल के दौरान हुई थी। मैं उनके सृजनात्मक ऊर्जा की खुले मन से प्रशंसा करता हूँ। उनके चित्र प्रत्येक लोककथा की मूल संवेदना के बखूबी चित्रण में सफल रहे है। मुझे विश्वास है कि यह सचित्र पुस्तक पाठकों के लिए रुचिकारक तथा वर्तमान में पूर्वोत्तर आधारित लोकसाहित्य की अन्य पुस्तकों से भिन्न एवं विशेष होगी। यह पुस्तक भारतीय साहित्य की व्यापक परिधि पर स्थापित सीमांत राज्य अरुणाचल प्रदेश की युवा पीढ़ी की सृजनात्मक शक्ति का परिचायक है। इंदिरा गाँधी राष्ट्रीय मानव संग्रहालय,

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Power line interference noise cancellation in ECG using Zero Phase IIR Notch filtering

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Rajiv Gandhi University, India

ABSTRACT
The presence of powerline interference noise in ECG signaldegrades the quality of signal, which may alter the original characteristics of the ECG signal. In this paper digital IIR notch filter with zero phase filtering technique is proposed to eliminate the powerline interference noise in the ECG signal. There after correlation coefficient is calculated between the filtered ECG signal and standard input ECG signal for its validation. The quality factor of digital notch filter is also tuned to achieve the better correlation coefficient and SNR of filtered ECG signal. We found highest correlation coefficient of 1 and lowest coefficient of 0.9999 at quality factor of 1 and 3 respectively. Further this method is validated on MIT-BIH arrhythmia database.

Keywords-Powerline Interference, ECG signal, IIR notch filter, Zero phase filtering

Impact of IoT Technologies on Smart City Infrastructure: Current Applications and Future Potential

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ABSTRACT
With the advent of digitization, upcoming technologies like Internet of Things (IOT) are being used by organizations to manage their business, infrastructure as well as assets. In order to make the IT Infrastructure more efficient, upcoming technologies like Internet of things play a very important role as IoT has increased the scale of the storage and the server spaces, improved the internet connectivity thereby leading to a smarter IT infrastructure. Although IoT adoption is taking place rapidly at the enterprise and industrial level; there is a dearth of academic literature in this area. Hence the objective of the paper is to study the adoption of various IoT technologies for smart city infrastructure, understand the impact/benefits of these technologies and propose future potential applications which can be used for smart infrastructure. A case study approach has been adopted for this research wherein various use cases in the IT industry have been analysed with respect to the adoption of IoT technologies for smart city infrastructure and the benefits of the same to the various sectors. The study will be useful for academicians, and practitioners, and Government officials to design and develop solutions for smart city infrastructure that will add to wellbeing of society at large..

Keywords—IoT, IT Infrastructure management, Smart City, Digitization

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Sonochemical Organic Synthesis

Edited by
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CHAPTER 1

Ultrasound-assisted organic synthesis

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1. Introduction

Traditional methods to carry out organic synthesis reactions face drawbacks such as long reaction time, non-satisfactory yields, more solvent, toxic/costly reagent requirements and high temperatures and on the other hand, results in uneconomical products. Use of heterogeneous systems gives rise to mass transfer resistance issues depending on the number and type of phases present. It may also lead to agglomeration of particles which lowers surface area and eventually slows down the reaction rate. To overcome all these issues, the use of ultrasound (US) is a cost-effective method to intensify various reactions such as aqueous and nonaqueous homogeneous reactions, heterogeneous reactions, phase-transfer reactions, metal-organic frameworks, bio-enzymatic, among others.

Application of sound waves along with its chemical effects is termed as sonochemistry. The application of ultrasound waves was first tried in the early nineties by Richards and Loomis. This was followed by Schultes and Frenzel who studied the aqueous hydrogen peroxide formation at 540 kHz. Furthermore, in 1936, Schultes and Gohr observed that light could be produced by the high-intensity sonochemical reaction of liquids in the range of 190–750 nm wavelength. This phenomenon was termed as sonoluminescence. This long journey of sonochemistry has been remarkable after the 1980s, where cavitation phenomena was considered.

Ultrasound has been used as a process intensification tool, between 20 kHz and 5 MHz frequency range, for the removal of biologically active compounds nanoscale operations and formation of medicines. Chemical reactivity increases by ultrasound through the formation and collapse of cavitation bubbles in a liquid medium. The propagation of ultrasound waves takes place in a liquid medium in alternate compression as well as rarefaction and cavities are formed. Once the attractive forces of the liquid overcome by rarefaction cycle, the cavities grow to a maximum size and then burst resulting in energy dissipation (Fig. 1) [1–3]. Due to turbulence, corresponding with the liquid circulation associated with the creation and breakdown of the bubbles, mass transfer rates are improved. Whether ultrasound can be applied to accelerate the reaction chemically as well as physically depends on the local hot spots and by enhancing the mass transfer rates, respectively. In addition to improvement in mass transfer rates, it also gives better catalyst

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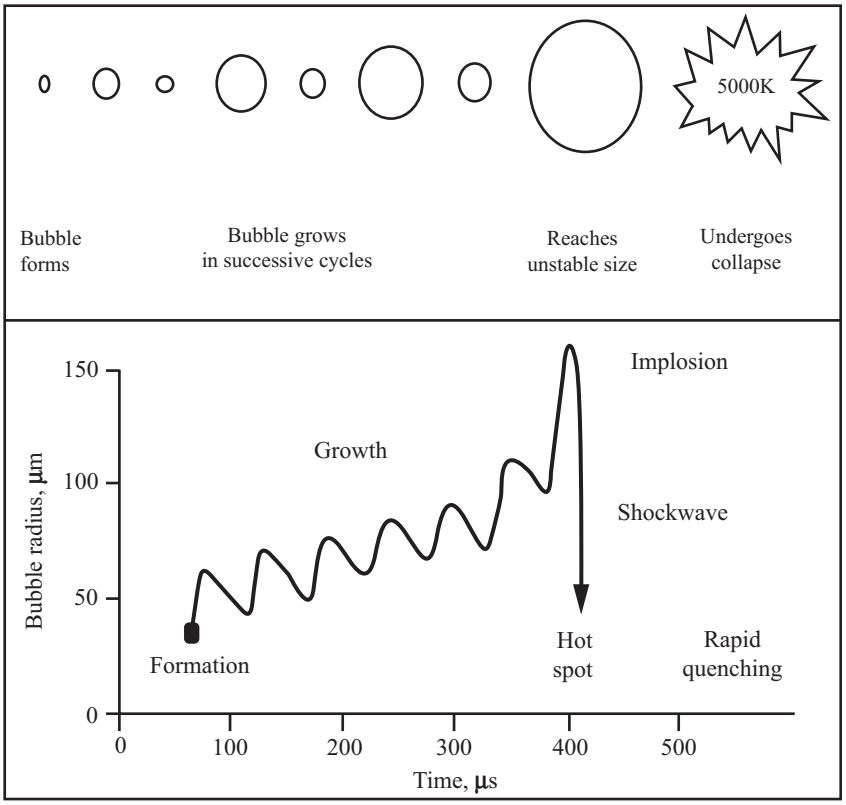


Fig. 1 Formation of bubble, development, and collapse. *(Reproduced with permission from P. Chowdhury, T. Viraraghavan, Sonochemical degradation of chlorinated organic compounds, phenolic compounds and organic dyes—a review, Sci. Total Environ. 407(8) (2009) 2474–2492.)*

effectiveness. Typically, the effects of cavitation in aqueous medium incorporate elevated temperatures (2000–5000 K), pressures up to 1800 atmosphere. Ultrasound is beneficial to accelerate chemical reactions by improving yields, lowering reaction times as well as increasing selectivity. Due to all these reasons, it has been popularized as a novel approach for the production of organic compounds since the past couple of decades [4]. Even though, the use of ultrasound is beneficial for laboratory-scale operations; for its commercial implementation for organic synthesis, there are some engineering concerns such as missing scale-up procedures, efficient designs [5].

2. Extrinsic variables affecting ultrasound irradiation

The intensity of cavitation produced by ultrasound is dependent on various parameters. These parameters not only add in the cost of the process but also decide the scale-up of

the reactor. Thus, it is essential to optimize these parameters for the particular system to get maximum yield at minimum cost. While carrying out US-assisted reactions, it is advisable to study the following parameters for the development of new analytical applications.

2.1 Influence of solvent

The change in solvent also changes the physicochemical properties, i.e., density, vapor pressure, surface tension, and viscosity which affects cavitation intensity, but chemical reactivity of the solvent has an intense effect on ultrasonication. The secondary reactions of sonolysis of water vapor between $OH^{\bullet}$ and $H^{\bullet}$ explain aqueous ultrasonication. At elevated temperature, solvent does not show inert behavior. It can be overcome by application of low vapor pressure solvent (except halocarbons) which reduces their concentration in the vapor phase of ultrasonication. In order to lower the viscosity of the medium, the solvent plays an important role by making it uniform and miscible [6]. Therefore, the selection of solvent has great importance in ultrasound irradiation.

The polarity of the solvent, along with denaturation conditions are the parameters that need to be considered while selecting the solvent for US-assisted enzymatic reactions. In a comparison of oil with methanol as a reactant/solvent for the synthesis of biodiesel, the bubble gets collapsed at a higher rate in methanol than that of oil. As the viscosity of methanol is lower than oil, the rate of bubble collapse in more in methanol. Therefore, methanol is preferred as a solvent in case of biodiesel formation due to the advantages of enhanced interfacial area and rate of reaction [7].

2.2 Influence of power

Chemical effects on a reaction can be caused by supplying sufficient acoustic energy so that the cavitation threshold of the medium is overcome. "Cavitational zone" is the region where cavitation occurs around the radiating source. This enhances with increasing intensity of dissipation. Cavitational intensity can be increased by increasing ultrasonic power. Also, with an increase in power, enhancement in the rate of reaction is observed and due to continuous use of power for a long time, rate of reaction decreases [8] which results in the generation of the cloud of cavitation bubble around the probe. Collapsing of those cavitation bubbles takes place near high power dissipation [9]. With an increase in exposure time, bubble formation, as well as implosion, increases. Also, due to prolonged use of ultrasound, denaturing of catalyst along with the transducers occurs [10]. The reactor configuration and its specific application are the parameters responsible for optimum power dissipation [11]. Acoustic energy present in reaction mixture gets decreased due to decoupling losses [12].

Overall literature hypothesizes that frequency, duty cycle, catalyst loading, and molar ratio are the important parameters. By keeping them constant, the influence of ultrasonic

power in organic synthesis has been optimized. Effect of power on the release of iodine by sonolysis of aqueous KI was reported [13]. Also, the initial power dissipation was proportional to iodine release, till 40 W and remained constant till 100 W which dropped significantly after 100 W.

Enzyme catalyzed reactions, prefer lower optimum power dissipation because enzymes show the negative effect at higher power dissipation. Several reports such as [14] lipase catalyzed esterification reaction of methyl caffeate (MC) with methanol along with caffeic acid using Novozym 435 under the influence of ultrasound irradiation have been reported. The impact of power on reaction has been studied by the increase in power under pulse mode at 25 kHz frequency and temperature of 5°C which resulted in enhanced yield (99% conversion) at 150-W power dissipation under the time interval of 9 h.

In the case of heterogeneous reactions, a similar trend was repeated, which showed 93% yield (highest) at 75 W as optimum power dissipation. Beyond 80 W, there was no further improvement observed. The influence of ultrasonic power on the formation of methyl butyrate catalyzed by amberlyst-15 over the range of 50–145 W input power at 22 kHz frequency was studied [15], where the enhancement in conversion, till 100 W was observed and beyond that conversion, was found to decrease.

All the above-reported trends show that with an increase in power dissipation up to a certain optimum value, conversion of the US-assisted organic synthesis reactions reaches the maximum value. Beyond certain optimum power dissipation, conversion gets reduced, which depends on the specific class of reaction carried out. Therefore, the reactor configuration, i.e., number and position of the transducers and the type of reaction are the factors on which optimum power dissipation would be dependent. Laboratory-scale investigations in reactors which are almost same as the design of the commercial-scale unit can give rise to the actual value of power dissipation.

2.3 Influence of frequency

Ultrasonochemical waves produce frequencies in the range of 16–100 kHz which enhance the cavitation effect. Frequency acts as the origin of the dramatic impact of power dissipation on chemical reactivity. In the case of radical formation mechanism, higher frequencies are preferred as they facilitate and accelerate a given reaction.

The bubble formation is proceeded by passing ultrasonic waves via a medium which begins with growth and disruption of the bubble [16]. The classification of ultrasonic frequencies has been done based on its large-scale operation in three groups such as power ultrasonication (16–100 kHz), high-frequency ultrasonication (100 kHz–1 MHz), and diagnostic ultrasonication (1–10 MHz) [17]. When negative pressure of the rarefaction exceeds the attractive forces between the molecules of the liquid, voids get formed. As the frequency increases, cavitation goes on decreasing, due to less pressure produced

by rarefaction cycle which is required to attain cavitation and sometimes the rate of the compression exceeds the duration which is required for the collapsing of bubbles [18]. Therefore the main phenomena of acoustic streaming arise where cavitation produced by ultrasonic waves having frequency 16–100 kHz results in the formation of larger cavitation bubbles with elevated temperature and pressure conditions [19]. In the case of homogeneous liquids, frequency plays an important role to attain optimum cavitation because homogeneous ultrasonication is carried out beyond optimum (offset) value. To overcome this counteracting behavior, there is a need to specify an optimum range of frequencies.

In the sonochemical degradation of carbon tetrachloride, the authors have claimed that at 500 kHz, the higher degradation rate is observed as compared to 20 kHz. Similarly, decomposition of chlorobenzene and removal of 2-chlorophenol was reported [20, 21] which demonstrates that for radicals, higher frequency is preferable as dominant chemical effects occur that particularly intensify the oxidation reactions where a major controlling factor is the hydroxyl radicals. For heterogeneous reactions, the opposite trends have been observed in the literature.

Also, the synthesis of 4-methyl cinnamoyl glycerol using enzyme over the frequency of 20–40 kHz in 48 h has been reported. As frequency increases from 20 to 35 kHz, conversion increases and beyond 35 kHz, it decreases because at this frequency deactivation of the enzyme occurs, due to physical effects and high shear forces [22].

Overviewing these literature trends, it can be said that for enzymatic reactions or heterogeneous reactions, frequencies in the range of 20–50 kHz are preferred. Physical effects are required in order to eliminate mass transfer resistances and to retain the catalyst activity. Similarly, in the case of homogeneous reactions or heterogeneous reactions, which involve radical mechanisms, higher frequencies (200–500 kHz) result in enhanced reaction rates [23].

2.4 Influence of duty cycle

The existent exposure time of ultrasonication in one cycle is known as the duty cycle. The ON/OFF time of ultrasonication can be adjusted to change the duty cycle [24]. Formation of the bubble takes place in ON time whereas its enlargement is carried out in resting time (OFF time). In US sonochemistry, the conversion of a product increases as the duty cycle increases. At the same time, it might affect the transducers, which lead to wear and tear effects. To avoid this effect, another type of transducers such as pulse mode is reported [25, 26]. In order to enhance the transducers life, the reaction should carry out at minimum duty cycle.

Also, keeping the ultrasound "on" for a long time can damage the transducers, thus using recent instruments with better quality transducers should be preferred [27, 28].

Similarly, reports have been validated [25] that with an increase in the ultrasonic duty cycle, enzyme activity gets reduced as a result of the physical effects of shear and turbulence. The synthesis of isoamyl butyrate has been studied [29], where 83% as an optimum duty cycle has been reported. The same result of an optimum duty cycle in heterogeneously catalyzed formation of methyl butyrate has been reported [15] and investigated that with an increase in the duty cycle over the range of 25%–75%, conversion increases from 72% to 91.64% and as observed, beyond 75% duty cycle, conversion gets reduced. Typically, it can be established that depending on the configuration of the reactor along with the type of reaction system in the presence of a catalyst, the optimum duty cycle would be intensified to obtain benefits of ultrasound operations.

2.5 Influence of temperature

Though temperature and the choice of solvent are interrelated variables, both are essential. With a rise in solvent vapor pressure, the maximum bubble collapse temperature and pressure decreases. Therefore, in a reaction where sonochemical activation takes place through cavitational collapse and a low-boiling solvent is present, low temperature is beneficial. Conversely, high boiling solvents are preferred where reaction requires elevated temperatures. In the case of heterogeneous reactions, an external surface of a catalyst or an inorganic solid reagent gets affected by sonication where a balance should be maintained so that proper cavitation takes place as well as the thermodynamics of the reaction does not get affected. Also, the energy required to initiate cavitation is enhanced by applying external pressure to a reaction system, which ultimately enhances the hydrostatic pressure of the liquid. The highest temperatures and pressures can be faced at the time of bubble collapse when threshold energy exceeds the available irradiation source and corresponding hydrostatic pressure increases the sonochemical effect.

In US-assisted reactions, the effect of bulk liquid temperature is also dependent on the temperature of the counteracting reagent [9]. With a rise in the reaction temperature, chemical kinetics get enhanced as in the case of conventional reaction systems, but the cavitational intensity decreases. An inverse effect of temperature on cavitation intensity takes place due to formation of vaporous cavities, which reduces bubble collapse [30].

Novozyme 435-assisted hydrolysis of soybean with the help of methanol (1:6) using 40 kHz frequency has been reported [31]. The reaction was carried out over the range of 30–70°C, and the highest activity was observed at 40°C and reduced beyond 40°C, which might be due to decrease in viscosity at higher temperatures which improves emulsification. Infinitesimal increase in temperature causes the better collisions of enzyme along with the substrates which result in enzyme-substrate complex with increased enzyme activity at 40°C [32].

From the above examples, it can be effectively concluded that the maximum rate of reaction can be obtained at an optimum temperature. In US-assisted organic

homogeneous or heterogeneous chemical synthesis, due to reduced cavitational activity, the conversion gets reduced as well as in US-assisted enzymatic route, a lower temperature is preferred as an optimum temperature. Beyond this value, the reduced rate of reaction is seen due to denaturation of enzymes at higher temperatures.

3. Origins of the chemical effects in sonochemistry

The earlier assumption about ultrasound was that it can be commonly used to assist the reactions associated with solid reagents only; this is not particularly correct. A large number of groups are seeking to achieve knowledge of sonochemistry, which can help them to anticipate the type of reaction affected by sonication. Luche has classified sonochemical reactions into three categories based upon the cavitational chemical effects. Other than chemical effects, there are some mechanical effects related to cavitation bubble collapse which are treated as physical effects and evaluated to be negative sonochemistry. Those negative effects are also significant, which have been used in the analysis and included in the below three reaction categories affecting sonochemical enrichment.

1. Homogeneous reactions involving radical mechanism are altered by ultrasound irradiation. However, sonication does not influence ionic mechanisms. In the homogeneous liquid system, the collapsing of the cavitation bubble leads to immediate inflow of liquid to cover the void space formed through the collapsing cavity. The rupturing of bonds in compounds takes place due to shear forces produced by this inflow in the surrounding bulk liquid. The similar effect has been observed in the reaction of polymeric material decomposed in the fluid [33] (Fig. 2).

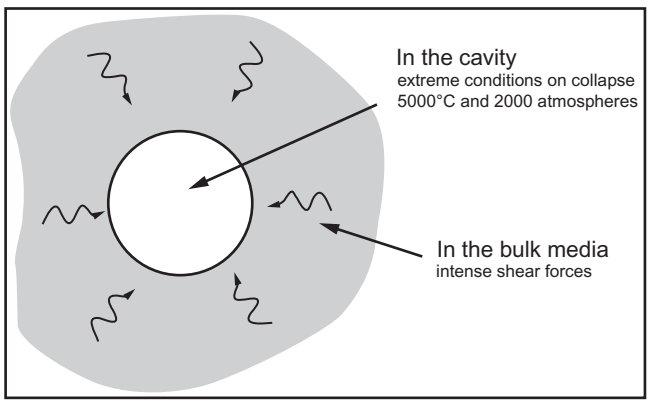


Fig. 2 Cavitation in homogeneous phase. *(Reproduced with permission from S. V. Sancheti, P. R. Gogate, A review of engineering aspects of intensification of chemical synthesis using ultrasound, Ultrason. Sonochem. 36 (2017) 527–543.)*

2. Heterogeneous reaction progresses via ionic intermediates. They are affected by a decrease in the particle size as well as enhancement in mass transfer rate, which are the physical impacts of cavitation. In such reactions, the selection of operating parameters is crucial due to less importance of the chemical effects of sonication.

   In phase-transfer heterogeneous reactions due to the collapse of a cavitational bubble, layer disruption along with the rapid blending produces ultrafine mixtures (Fig. 3). For maintaining stability, surfactants are employed in making the emulsion. Enhancement in the surface area occurs as a result of the generation of fine emulsions, giving the desired intensification. Due to cavitational effects, phase-transfer heterogeneous reactions require less catalyst.

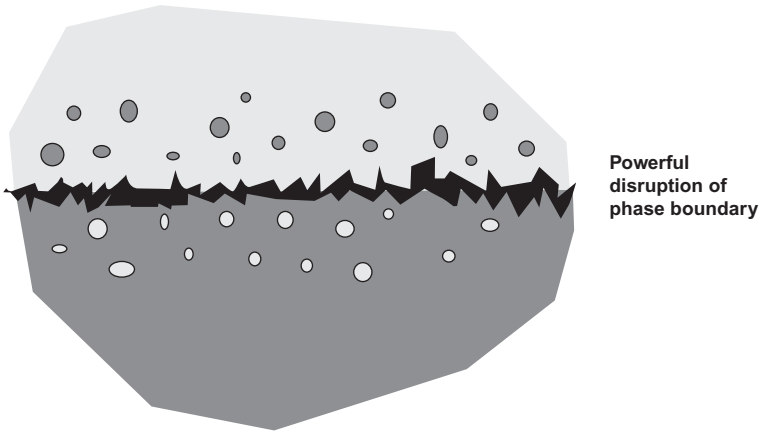


Fig. 3 Cavitation in dual-phasic liquid system. *(Reproduced with permission from S. V. Sancheti, P. R. Gogate, A review of engineering aspects of intensification of chemical synthesis using ultrasound, Ultrason. Sonochem. 36 (2017) 527–543.)*

3. The reactions that involve a radical mechanism or radical, as well as ionic mechanism, get influenced by sonication. Radical reactions are affected by the chemical effects of ultrasound irradiation, whereas ionic reactions are influenced by enhanced mass transfer rates.

   For heterogeneous systems in the presence of solids, the bubble collapse may be symmetric or asymmetric. The size and type of the material in shock waves raise the motion of solid particles in solution. The breakdown of the bubble due to such a motion of solid particle results in the availability of increased area for reaction and activation of the catalyst can also be done by physical effects. That results in the cleaning of the surfaces and also enhances transport rates that depend on the interruption of the boundary layers (Fig. 4).

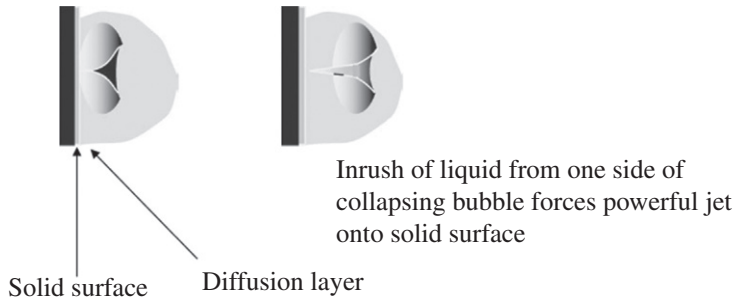


Fig. 4 Cavitation in heterogeneous systems. *(Reproduced with permission from S. V. Sancheti, P. R. Gogate, A review of engineering aspects of intensification of chemical synthesis using ultrasound, Ultrason. Sonochem. 36 (2017) 527–543.)*

4. Reactor design and configuration

There are many devices available to carry out ultrasonic irradiation. They are known as sonochemical reactors. The classification of sonochemical reactors depends on the nature of irradiation like direct and indirect. Direct mode refers to the direct contact of ultrasonic transducer with the reaction medium. In indirect mode, it refers to either a contact between separate reactor having reactants, which is suspended into ultrasonic vessel filled with a coupling liquid or sonication vessel itself containing liquid mixture. Sonochemical reactors are generally divided into three designs.

1. Ultrasonic cleaning bath.
2. "Cup-horn" sonicator.
3. Direct immersion ultrasonic horn.

In all cases, the original source of the ultrasound is a piezoelectric material, usually a lead zirconate titanate ceramic (PZT), which is subjected to a high AC voltage with an ultrasonic frequency (typically 15–50 kHz). The piezoelectric source expands and contracts in this electric field and is attached to the wall of a cleaning bath or to an amplifying horn.

4.1 Ultrasonic cleaning bath

For the indirect irradiation, a sonication bath is a very frequently used sonochemical reactor. It is an inexpensive instrument in which the ultrasound is applied with the help of transducers (Fig. 5). It is used primarily in laboratory ultrasound operations of US-assisted heterogeneous systems. A very less amount of energy is supplied to the actual reaction mixture within the medium as compared to ultrasonic horn (which are used in direct irradiation mode). Depending on the size of the vessel and the number of transducers, distribution of the cavitational activity takes place in the case of ultrasound bath.

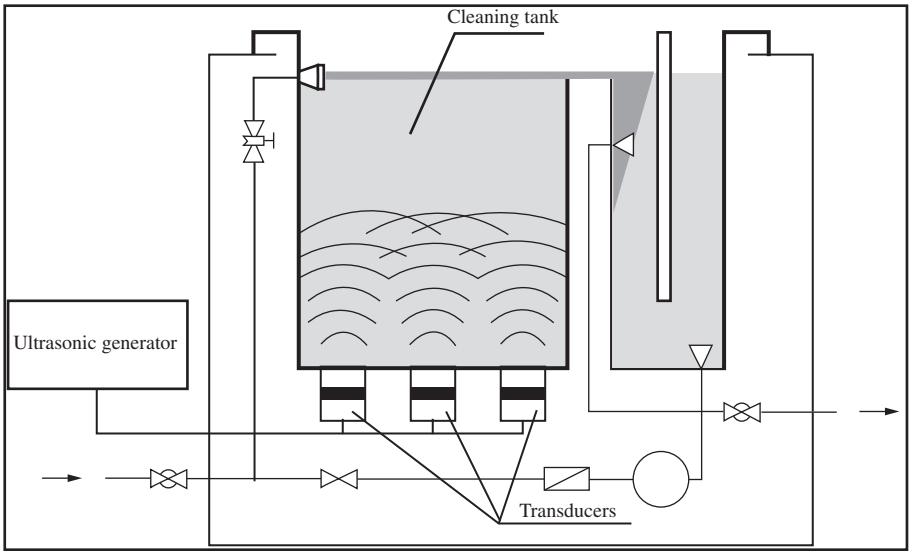


Fig. 5 Ultrasonic cleaning bath. *(Reproduced with permission from E. M. Hussein, K. S. Khairou, Sonochemistry: synthesis of bioactive heterocycles, Synth. Commun. 44(15) (2014) 2155–2191.)*

Along with the benefits of ultrasound bath, there are several potential drawbacks like variable acoustic intensity. It varies from bath to bath and one manufacturer to another. Therefore, the issue of replicability from one bath to another may arise. Also, the placement of the reaction flask, temperature, the height of both the bath liquid and of the solution within the reaction vessel are critical parameters [34, 35]. Coolants are used for thermostating, as they are passed through copper coils without contacting walls. In the case of homogeneous liquids, marginal acoustic intensities are present for the generation of cavitation. Also, in case of solids, the tensile strength of the liquid at the interface causes the cavitation well below thresholds as compared to simple solutions. However, for heterogeneous ultrasound irradiation, the sonication bath can be considered with limited potential.

4.2 "Cup-horn" sonicator

To get high cavitational intensity at low operating volumes, ultrasonic horns are most commonly used for laboratory-scale operations. By keeping the frequency of irradiation constant, the power dissipated within the reaction mixture can be varied with an introduction of the acoustic energy directly into the liquid. The diameter of the probe and the height of the liquid in the reactor are the controlling factors in terms of cavitational activity and application point of view. There is a certain limitation in the case of the horn

system where contamination should be strictly prohibited. Due to extensive use of higher levels of power dissipation, erosion of metal takes place into liquid along with the pitting of the tip [36]. Also, the shape of the horn controls the cavitational activity along with the transfer of energy considering the minimum effect on the surface erosion. Cup horns are a known modification where a small sonication bath is driven by a horn extending through its base (Fig. 6). Initially, it was used in cell disruption, but nowadays it has found application in sonochemistry in indirect irradiation, but more power dissipation occurs in comparison with the typical sonication bath. An ultrasonic horn is much better with higher capability for processed volume. In the case of ultrasonic probe in standard piezoelectric transducers, it is made up of Titanium crucible. In comparison with ultrasonic cleaning bath, it is advantageous in terms of acoustic intensities, frequency control, as well as thermostating capacity. As there is no contact between radiating surface and reaction solution, the resulting intensities are smaller than that of direct immersion ultrasonic horn. Therefore, homogeneous ultrasound irradiation is disadvantageous in terms of activeness. But it is also advantageous as it is free from contamination against the erosion of the titanium horn.

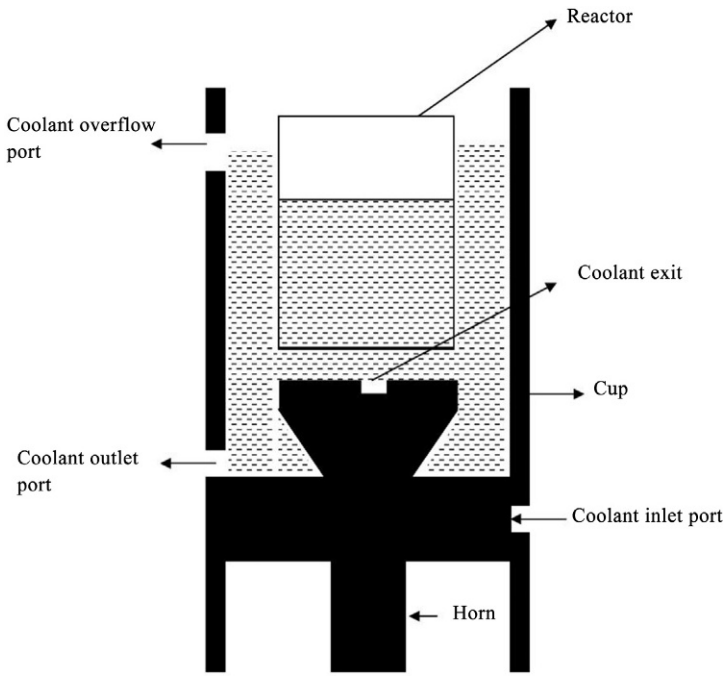


Fig. 6 Ultrasonic probe Cup horn. *(Reproduced with permission from P. Chowdhury, T. Viraraghavan, Sonochemical degradation of chlorinated organic compounds, phenolic compounds and organic dyes—a review, Sci. Total Environ. 407 (8) (2009) 2474–2492.)*

4.3 Direct immersion ultrasonic horn

It is a very powerful ultrasonic reactor specially used in a chemical laboratory in an inert atmosphere (Fig. 7). Like a cup horn, direct immersion ultrasonic horn is also designed by biochemists for cell disruption. It is readily available at a reasonable cost. Even variable shapes of titanium horns and sizes of power supply are provided.

For large-scale operations, the use of direct immersion ultrasonic horn provides the flexibility of operating at multi-liter capacity. This horn gives high and variable intensities at a frequency of 20 kHz. Due to more power dissipation, the necessity of temperature controller to cool down the reaction arises which depends on the type of configuration. Also, it shows the drawback of erosion of the titanium tip without chemical effects, which shows enhanced tensile strength with less reactivity of Ti metal. The commercial application of these horns involves cell disruption on large scale, degassing of liquids, dispersion of solids into liquids, and emulsification of immiscible liquids. The direct immersion ultrasonic horn is most widely found in industrial ultrasonic reactions than at the laboratory scale.

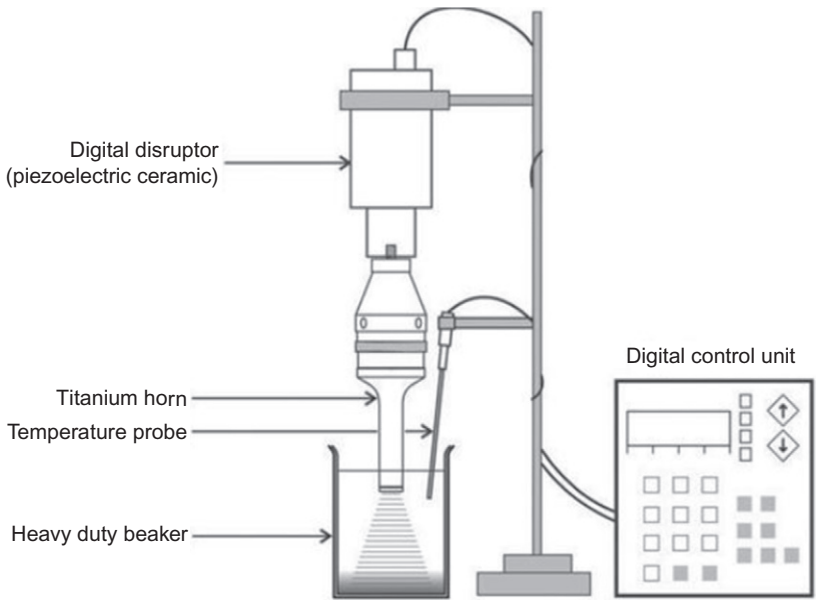


Fig. 7 Direct immersion ultrasonic horns. *(Reproduced with permission from E. M. Hussein, K. S. Khairou, Sonochemistry: synthesis of bioactive heterocycles, Synth. Commun. 44(15) (2014) 2155–2191.)*

5. Classification of US-assisted organic synthesis

Application of ultrasound for intensifying different processes results in various organic synthesis reactions. The use of highly intensive sonochemistry in aqueous or nonaqueous medium gives benefits of benign reaction conditions, less time with enhanced yield, which mostly depends on physical effects that take place in ultrasonication. Here, we are classifying reactions into homogeneous and heterogeneous systems.

5.1 Homogeneous

Sonochemical effects in homogeneous liquid systems, usually occur at different sites. Those sites are given below.

1. extreme conditions inside the collapsing bubble;
2. at the interface in between the cavity and present bulk liquid; and
3. in the bulk liquid where mechanical effects prevail.

Further, we will proceed with the classification of US-assisted homogeneous organic synthesis into aqueous and nonaqueous homogeneous systems. They depict the different type of cavitation event in each case.

5.1.1 Aqueous

Aqueous irradiation of organic compounds frequently gives rise to extremely oxidized or degraded products in multiple amounts. In the case of aqueous media, there is an overall deficiency of specificity for ultrasonic irradiation because while carrying out sonolysis of water, we tend to get intensely reactive intermediates at respectable rates.

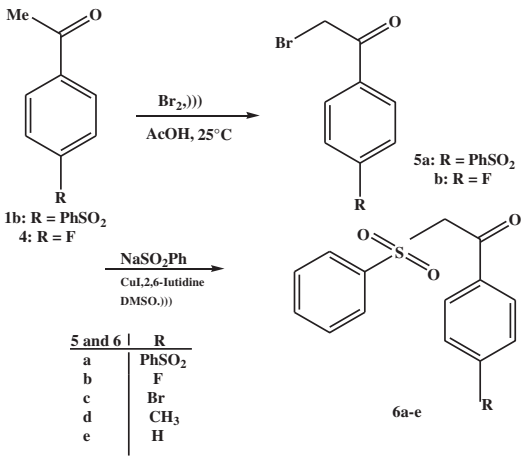
In 1982, aqueous sonochemistry was reported, in which stereoisomerization of maleic acid to synthesize fumaric acid by ultrasound irradiation using Br_2 was carried out. In this reaction, the frequency used over a very wide range and Br' is an efficient catalyst for the isomerization obtained from sonolysis, which makes this reaction unique in sonocatalysis, as given below.

$$Br'_2 \longrightarrow 2Br' +$$

There are many studies, which reported the effects of ultrasound through various solvolysis reactions. One of them applied in both ultrasound irradiation and catalytic wet peroxide oxidation for a breakdown of 4-hydroxy benzoic acid where the determination of enhanced rate for the hydrolysis of acetates and saponification of fats has been studied [37].

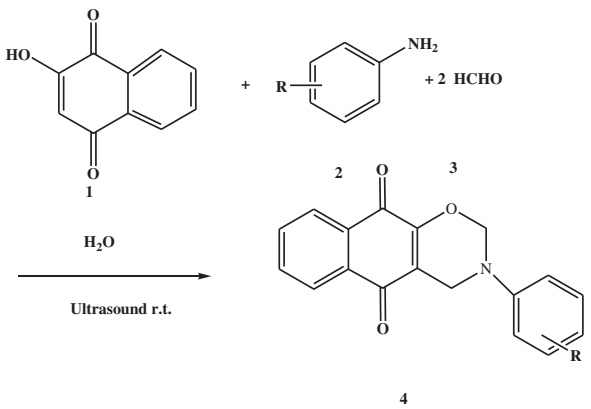
In 2013, the synthesis of Novel Homoallylic Alcohol Derivatives using water as a medium was established by comparing both conventional and US-Assisted approach [38]. The reaction was carried out in aqueous media, with different carbonyl compounds

with allylic bromides through US-assisted Barbier reaction. The α-bromoketones reacted with sodium benzenesulfinate in the presence of CuI/2,6-lutidine. Simply, sulfonation of α-bromoketones was carried out which produced β-keto-sulfones with satisfactory yields. Therefore, this aqueous media sulfonation reaction was beneficial in terms of excellent yields, lesser reaction time, and more simple in comparison with the traditional one (Scheme 1).



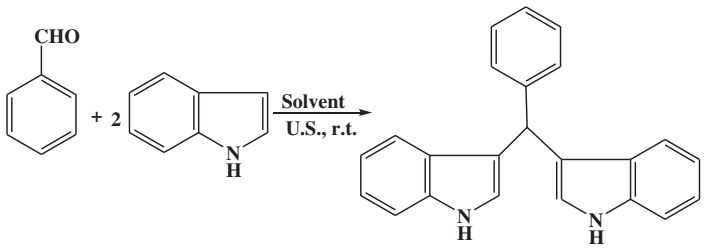
Scheme 1 Sulfonation of *α*-bromoketones in presence of ultrasonication.

In 2017, the formation of naphthoquinone combined oxazine derivatives under an aqueous medium by using sonication has been investigated [39]. Development of energy efficient, as well as the environmentally safe procedure, has been carried out through the reaction of 2-hydroxy-1,4-naphthoquinone, aromatic amine and formaldehyde in a single approach using water as an aqueous media under ultrasound irradiation (Scheme 2).

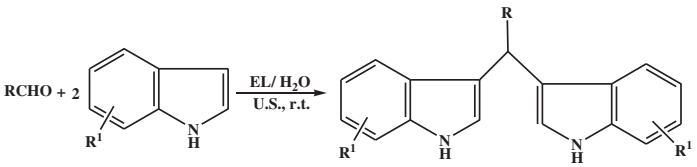


Scheme 2 Formation of naphthoquinone combined oxazine derivatives using ultrasonic irradiation.

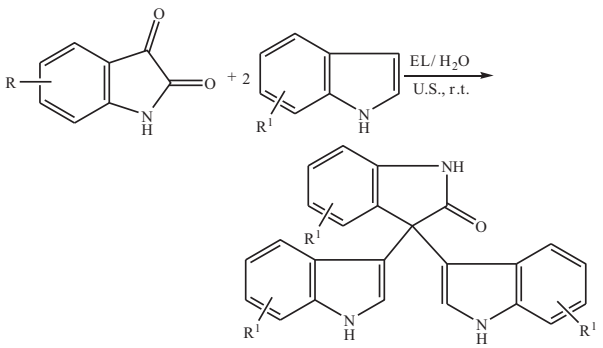
Later in 2017, synthesis of Bis (Indolyl)Methanes and 3,3-Bis (Indolyl) oxindoles in the catalyst-free medium using Aqueous Ethyl Lactate has been investigated [40]. In the reported approach, indoles reacted with aldehydes or isatins in water and ethyl lactate under the influence of ultrasonication. In addition to benefits of aqueous media along with the ultrasonication, this approach is free from the catalyst, having a broad substrate scope and applicable for industrial synthesis (Schemes 3–5).



Scheme 3 Ultrasound-assisted formation of Bis (Indolyl)Methanes.



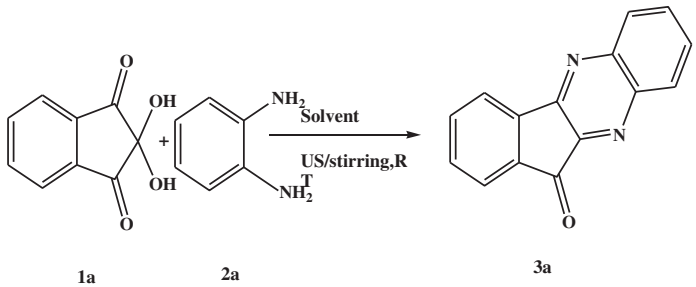
Scheme 4 Formation of Bis (Indolyl)Methanes in water and ethyl lactate using ultrasonication.



Scheme 5 Formation of 3,3-Bis (Indolyl) oxindoles in water and ethyl lactate using ultrasonic irradiation.

Also, in 2017, the latest achievements in the ultrasonically irradiated organic synthesis using aqueous medium have been reported [41]. There are several reports available on the application of an aqueous media in US-assisted organic reactions. Based on the knowledge of green chemistry, water is considered as the safest solvent as compared to others. Therefore, it is a sustainable approach that holds an active association between highly intensive ultrasonication and aqueous medium. Also, the application of ultrasound irradiation along with the water leads to an eco-friendly protocol.

Recently in 2019, the formation of crucial heterocycles such as Quinoxaline, 1,4-oxazine, 1,4-thiazine, and 1,4-dioxin derivatives using catalyst-free medium in water under the influence of ultrasonication has been studied [42]. There were various methods reported for the synthesis of the same. However, these methods have certain drawbacks. Therefore, for the synthesis of these heterocyclic compounds, easy and energy-efficient methods are required (Scheme 6).



Scheme 6 The reaction of ninhydrin and o-phenylenediamine in presence of ultrasonication.

Therefore the application of water as a solvent than other volatile organic solvents is appreciable in green chemistry [43–46]. However, aqueous medium gives increased reaction rate as a result of strong hydrogen bonding. Also, the ultrasound using water offers benefits of nontoxicity, recyclability with the purification of products [47–52]. Nowadays, catalyst-free aqueous medium has gained importance in laboratory scale as well as industrial-scale due to properties like rapid, energy-efficient, cheap, improved selectivity, environmentally benign, and easy isolation of product [53, 54].

5.1.2 Nonaqueous

Homogeneous nonaqueous sonication was not reported frequently until the past few years. In 1937, Porter studied the sevenfold acceleration due to Curtius rearrangement of $C_6H_5CON_3$ to C_6H_5NCO and N'_2 [32]. Later in 1965, Weissler has reported some solvents which are too slow in degradation like CH_3CN and $CC1_4$ [34]. In 1967, the initiation of explosions of tetranitromethane and nitro glycerine was investigated. Also, in 1974, the depolymerization of high molecular weight polymers was observed [55]. Principally, aqueous solutions with volatile organic solvents have not been reported for sonochemistry.

This led to a general belief that water can only act as a high tensile strength liquid to support intense cavitational collapse. Due to high vapor pressures, a large group of organic liquids reduces the strength of cavitational collapse. But it has now been established that cavitation will be accomplished by organic liquids via free radicals at low temperature through bond homolysis. In 1983, the sonolysis of alkanes has been studied, which is the same process as extremely high-temperature pyrolysis. Also, in 1979, the sonolysis and pyrolysis of biacetyl, which produces acetone, has been reported and compared with the sonolysis and radiolysis of menthone in 1980. The chemistry involved in nonaqueous sonochemistry can be tedious, as seen in the tarry polymerization of various substituted benzenes reported by several authors. The results obtained from the analysis of aqueous sonochemical reactions are challenging to understand because of the complication of the secondary reactions. Therefore, in the case of nonaqueous liquids, the rates of degradation can be adjusted to slow down quite below than water by proper selection of solvent as well as by maintaining low volatility. Highly stable liquids can be obtained at lower temperatures like decane at $-10°C$. It is advantageous because instead of the secondary reactions occurring with solvent fragments; the primary ultrasound irradiation of decomposed substrates can be investigated. In future aspects of sonochemical studies, we can look forward to increase the use of nonaqueous sonochemistry with the application of low-volatility organic liquids.

5.2 Heterogeneous

The hastening of heterogeneous reaction using ultrasound is an emerging technique. It is accompanied by physical effects such as formation of emulsions at liquid-liquid interfaces, cavitational erosion and finally, purification takes place at liquid-solid interfaces. As the formation of shock wave damages as well as deforms solid surfaces, the surface area of friable solids gets increased.

The heterogeneous sonochemical reaction is a very known type of US-assisted reaction, in organic or organometallic chemistry. Further, US-assisted reactions can be applied to the leaching process to intensify their effect on leaching. Heterogeneous US-assisted reactions are further divided into three categories, which are stated below.

5.2.1 Metal-organic frameworks

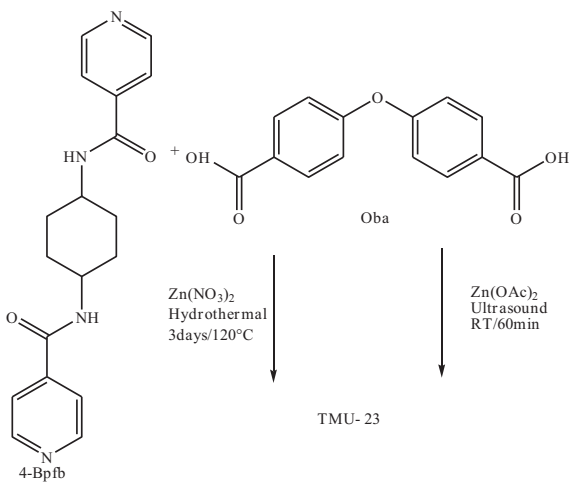
Material scientists have newly developed a porous material known as metal-organic frameworks (MOFs). In MOF's, metal ions together with organic multidentate ligands, are bounded through coordinate bonds. These organic-inorganic hybrid compounds are crystalline in nature. They provide high surface areas with better functionality, pore size, selectivity range of shape/size, and improvement in activity as compared to base metal oxides. However, they have application as a host in a variety of guest molecules [56–58], further used in adsorption, catalysis, magnetism, sensing, and drug delivery [59–61]. Nature of the metal-organic framework decides the physical parameters of MOFs like magnetic susceptibility, conductivity, and optical characteristics [62]. MOF's act as a bridge between zeolites (having small pore size) and silicates (possess huge size). MOF's exhibit reduced chemical, thermal, and hydrothermal stability in comparison with other oxides [63].

For the manufacturing of MOF's, transition metals, alkaline earth metals, p-block elements, actinides as well as mixed metals are used since the past two decades. It can be prepared by low vapor diffusion and solvothermal techniques [64] but need to be maintained at elevated temperature and pressure. Therefore, nowadays, nanoparticles with particular morphologies are synthesized by the US-assisted method [65, 66].

In 2016, the most simple and commercial method for the formation of nano MOFs using ultrasonic sonochemistry has been reported [67]. Recently in 2018, Ultrasound-assisted amide functionalized metal-organic framework used for nitroaromatic sensing. While synthesizing nanoplates of zinc (II)-based MOF's through the ultrasonic method, surfactants were not involved at ambient temperature and atmospheric pressure. Therefore, Field Emission Scanning Electron Microscopy (FE-SEM), powder X-ray diffraction, thermogravimetric analysis (TGA), elemental analysis, and FTIR spectroscopy are the methods used to analyze increased control of particle size and morphology. Similarly, by using different precursor concentration, amide-functionalized nano metal-organic framework, $[Zn_2(oba)_2(bpfb)]\cdot(DMF)_5$, TMU-23, ($H_2oba = 4,4'$-oxybis(benzoic acid); bpfb = *N*,*N*′-bis-(4-pyridylformamide)-1,4-benzenediamine, DMF = *N*,*N*-dimethyl formamide), was reported by application of ultrasound sonochemistry. Also, the decrease in florescence intensity and an increase in selectivity of sensing capacity of nitroaromatic compounds like nitrophenol, nitroaniline, and nitrobenzene in acetonitrile solution is investigated [68] (Scheme 7).

5.2.2 Phase-transfer catalysis

Mutually insoluble compounds react with each other through phase-transfer catalysis (PTC). Since it is used in the synthesis of pharmaceuticals, agricultural chemicals, flavorings, dyes, perfumes, and environmental processes; it was attempted to improve the

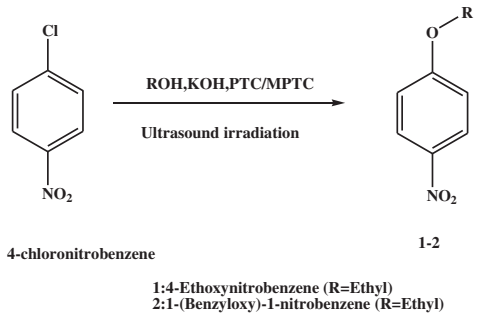


Scheme 7 Synthesis of TMU-23 via both ways hydrothermal as well as ultrasonication.

phase-transfer catalysts efficiency. "Multisite" phase-transfer catalyst (MPTC) is the newly developed PTC method, where catalytic efficiency has been increased, due to multiple molecules being able to be taken into the organic phase in one cycle [69–73]. As ultrasound sonochemistry reported advantages like high reaction rate, yield, and selectivity; therefore, its applications in organic synthesis has been predominant. The combination of PTC, along with ultrasonication has been formed to be an effective method for organic conversion [74–78]. Also, PTC assisted by sonication gives benefits of high mass transfer rate. In 2000, Cannizzaro reaction carried out by phase-transfer catalysis with sonochemistry has been estimated that the reaction rate increased by 20-kHz ultrasonic wave [79]. In the case of epoxidation and dichlorocyclopropanation of 1,7-octadiene and ethoxylation of p-chloronitrobenzene by phase-transfer catalyzed ultrasonication, increased rate of reaction was observed [80–82]. Phase-transfer catalysts carried by highly intense ultrasonic waves also promotes Williamson ether synthesis. Due to its potential and versatile technology, ultrasound has earned importance in polymerization industries [83], homopolymers, block copolymers [84], hydrogels [85], and polymer-inorganic composites, etc. [86]. Liquid-liquid phase-transfer catalysis (LLPTC) combined with ultrasound irradiation also enhances the rate of reaction, but from an application point of view is rarely seen in the literature.

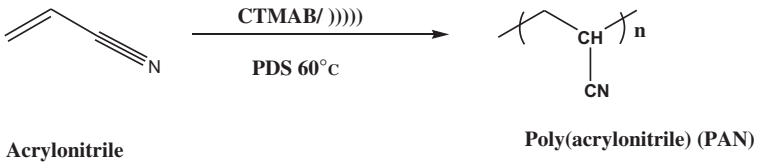
However, the application of PTC along with ultrasound method, has achieved exceptional attention in both the commercial as well as academic point of view, due to its strong and flexible nature. It also provides multiple benefits that favor its use in different polymerization techniques to synthesize polymers. To the best of our knowledge, the combined approach of PTC and ultrasound is limited.

In 2017, the novel processes in phase-transfer catalytic reactions under the influence of ultrasonication have been studied [87]. The enhanced yield at reduced organic solvent and less reaction time was reported. The ethoxylation reaction, in which 4-chloronitrobenzene reacts with potassium ethoxide has been evaluated in the presence of PTC using ultrasound irradiation conditions (28 kHz, 200 W), that resulted in ethoxy-4-nitrobenzene (Scheme 8)



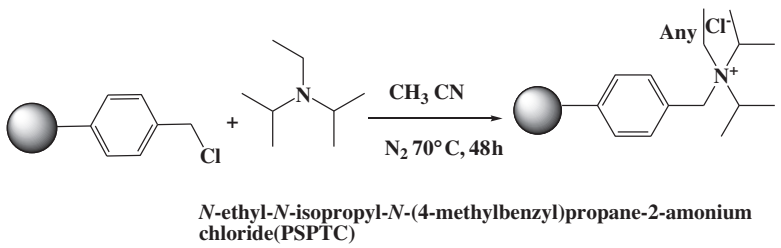
Scheme 8 Ultrasound-assisted reaction of 4-chloronitrobenzene with potassium ethoxide in presence of PTC to form ethoxy-4-nitrobenzene.

Later in 2017, ultrasonication conditions along with phase-transfer catalyst boosting up the rate of polymerization of acrylonitrile in a dual-phase system have been investigated [88]. The effect of various parameters like monomer, initiator concentration, catalyst and temperature, solvent polarity on the rate of polymerization was estimated, where the rate of polymerization (R_p) was found to be doubled as compared to silent condition. Also, activation energy (E_a) and other thermodynamic parameters were considered, and a suitable kinetic model was fitted (Scheme 9).

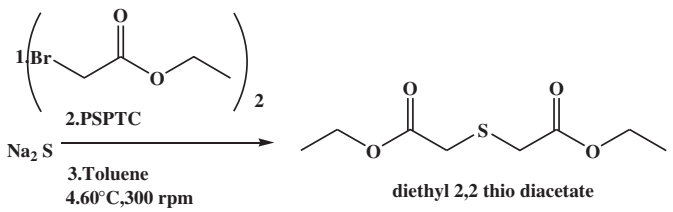


Scheme 9 Polymerization of acrylonitrile under ultrasonication using PTC.

Also, in 2015, formation of diethyl-2,2′-thiodiacetate with 2-bromoethylacetate using the latest polymer-supported phase-transfer catalyst under ultrasound irradiation has been studied [89]. The novel polystyrene-bound single-onium phase-transfer catalyst has been synthesized and explored its advantages in the synthesis of diethyl-2,2′-thio diacetate derivatives of thioether. Also, obtained high catalytic activity and reused benefits of catalyst with constant catalytic activity (Schemes 10 and 11).



Scheme 10 Synthesis of *N*-ethyl-*N*-isopropyl-*N*-(4-methylbenzyl)propane-2-ammonium chloride (PSPTC) in the presence of PTC using ultrasonication.



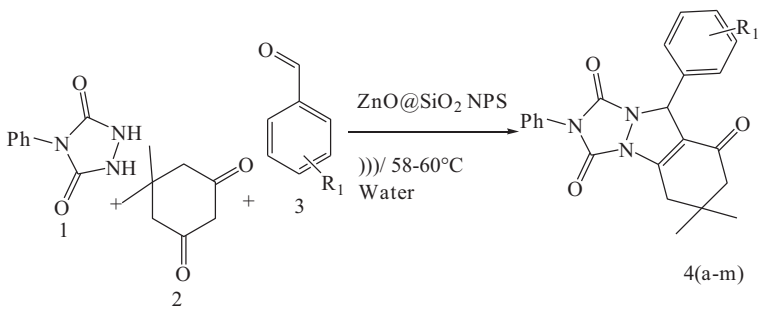
Scheme 11 Ultrasound-assisted synthesis of 2,2 thio diacetate in the presence of PTC.

5.2.3 Heterogeneous catalysis

In US-assisted organic synthesis, some catalysts get poisoned by the intermediates, slows down the rate of degradation, which restricts its potential usage. Those disadvantages can be overcome by using the US-assisted heterogeneous catalysis process. It is advantageous in terms of increasing the rate of degradation of the particularly targeted compound during processing. Also, it extracts product from the surface of the catalyst, which makes the clean and reactive catalyst surface ready to carry out further reactions [90]. In the polymer industry, CDNS (clodextrin nanosponge) are the most stable compound which works over a broad temperature as well as pH range and can form complexes with guest molecules of different hydrophobicity [91, 92]. Also, the solubility of aqueous media and sustainable release can be improved by using CDNS as a drug deliver [93, 94]. Therefore, CDNS is reported as effective support for the immobilization of catalytic species [95, 96]. Along with CDNS, Santa Barbara Amorphous, SBA-15, is also reported as support for heterogeneous catalysts.

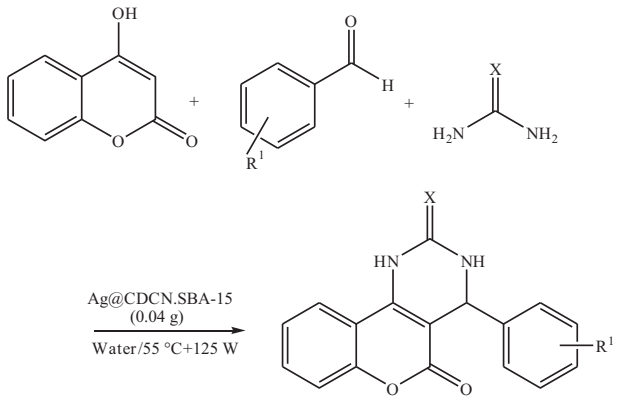
Initially, in 2016, a coupled ultrasound with heterogeneous Fenton process was investigated for the degradation of tetracycline using Fe_3O_4 catalyst [97]. Catalyst stability was investigated to be enhanced after application of ultrasound sonochemistry. The considerable reactive species during the process of oxidation were analyzed, which are surface hydroxyl radicals.

Also in 2017, synthesis of high-yield multicomponent triazolo[1,2-a] indazole-triones with silica-coated ZnO nanoparticles as a heterogeneous catalyst under ultrasound irradiation has been studied [98]. New approach for the synthesis of 4(a–m) triazolo[1,2-a] indazole-triones (TAITs) using the multicomponent condensation reaction among dimedone, 4-phenylurazole along with different aryl aldehydes in the presence/absence of SiO_2, ZnO, and SiO_2-coated ZnO (ZnO@SiO_2) nanoparticles (NPs) or nanorods as heterogeneous catalysts in deionized water (DIW) has been reported. Both catalyst and TAITs were beneficial in terms of environmental friendliness, efficiency, carefree handling, and cost (Scheme 12).



Scheme 12 Synthesis of 4(a–m) triazolo[1,2-a]indazole-triones (TAITs) with silica-coated ZnO nanoparticles as a heterogeneous catalyst under ultrasound irradiation.

Later in 2018, synthesis of Ag (0) nanoparticles immobilized on SBA-15/cyclodextrin nanosponge has been studied [99]. For the ultrasound irradiated production of benzopyranopyrimidines, SBA-15/cyclodextrin nanosponge was reported as an efficient catalyst. Due to beneficial features of SBA-15 and CDNS, they were applied for immobilization of Ag (0) nanoparticles where preparation and capping were done by using a bio-based approach. The analysis was done by using response surface methodology. The highest catalytic activity of Ag@CDNS-SBA-15 was obtained as compared to Ag@CDNS, Ag@SBA-15, and Ag@SBA-15 + CDNS. Reusability of catalyst up to four cycles was noticed where leaching of Ag (0) along with reduced catalytic activity was observed (Scheme 13).



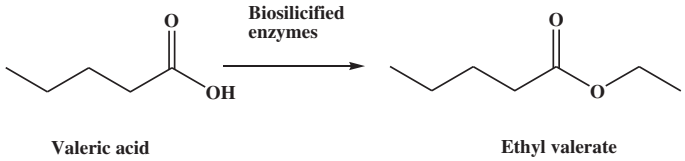
Scheme 13 Ultrasound-assisted production of benzopyranopyrimidines using SBA-15/cyclodextrin nanosponge.

5.3 Enzymatic catalysis

Accelerated growth in a field of ultrasound organic synthesis invites new routes and applications. Over the last decade, as compared to other routes, US-assisted organic enzymatic synthesis has acquired great importance. Food, biotechnology, and biopharmaceutical are the industries where enzyme-catalyzed US-assisted organic synthesis has gained diverse applications [100]. There is innovative convenience for the actual and novel products based on principles of Green chemistry and engineering. Generally, US-assisted enzymatic organic synthesis analyzes the reaction processes in terms of higher yield, short time, high mass transfer rates, better catalyst effectiveness. Additionally, it gives advantages like high selectivity, safer solvents, efficiency, better use of raw materials and catalyst making the process sustainable [101–103].

Recently in 2018, esterification of valeric acid to produce alkyl valerates using biosilicified lipases under ultrasound irradiation has been studied [104]. The reported technique is an innovative, environmentally benign, and sustainable approach. In this

ambient temperature technology, the lipases were of enhanced activity and more efficient among free enzymes. They have investigated parameters such as yield 90% in 2 h with 15% m/v of biosilicified lipase with molar ratio 1:2 (valeric acid: ethanol), which were better than free enzymes. Also, better reusability compared to free lipase was reported (Scheme 14).



Scheme 14 Esterification of valeric acid to produce alkyl valerates using biosilicified lipases under ultrasound irradiation.

Also, in 2017 the immobilization of pectinase using ultrasound irradiation within sodium alginate and further cross-linked with glutaraldehyde has been studied [105]. Increased in the activity of pectinase by 30.05% with enhanced immobilization yield of 92.28% was observed and verified by V_{max} and K_m (kinetic parameters). In the case of free pectinase, the thermal stability at 40, 50, and 60°C for 1 h was 31.98%, 19.90%, and 6.57% respectively, while it was 67.42%, 35.04%, and 19.71%, respectively, for immobilized pectinase.

Later in 2017, hyperactivation of cellulase immobilized on magnetic nanoparticles under the influence of ultrasonication has been investigated. After immobilization, enzyme MNPs were exposed to an ideal ultrasonic condition at 6 W, 24 kHz about 6 min. The enhanced catalytic activity of enzyme MNPs by 3.4 folds was reported, which can be associated with more interaction of enzyme-substrate complex. Furthermore, Ladole and coworkers have observed an enhancement in pH and temperature stability of cellulase @MNPs [106].

6. Kinetics of sonochemical reactions

An engineering aspect to understand the production and mechanism of the reaction is accomplished by establishing kinetic models. In the case of ultrasonically assisted reactions, rate constants are found to be much higher in magnitude in comparison with the traditional approach. The amount of catalyst, organic solvents, temperature, frequency, and power dissipation of the ultrasound waves are the dependent parameters to study the kinetics of the reaction. To study intensification of the kinetic rate constant, the understanding of the whole mechanism is necessary, as it is uncertain due to temperature variation in an ultrasound. Therefore, it is important to maintain the temperature constant even if very less (microsecond) time intervals with overall conditions being

ambient. The intense local heating and changes in activation energies are responsible for the enhanced kinetic rate constant.

6.1 Phase-transfer catalyzed reactions

In 2014, the kinetics of dual-site phase-transfer catalyzed dichlorocyclopropanation of *N*-vinyl imidazole was studied under US-assisted conditions with the help of highly alkaline base [107]. Further, it was investigated that, with an increase in alkaline conditions, the conversion of *N*-vinyl imidazole enhances initially and then reduces. Also, the K_{app} value increases with a corresponding increase in the operating conditions such as the weight of catalyst (*N*,*N*′-dihexyl-4,4′-bipyridinium dibromide), the concentration of substrate, agitation speed, temperature, etc. The estimated rate constant for pseudo-first-order US-assisted synthesis was much higher (fivefold higher) (frequency of 40 kHz, power dissipation of 300 W giving $K_{app} = 26.72 \times 0^{-3}\ min^{-1}$) than the conventional approach ($K_{app} = 4.98 \times 10^{-3}\ min^{-1}$). A kinetic study of C-alkylation of benzyl cyanide in the presence of phase-transfer catalyst with US-assisted approach was reported in 2014. The rate constants for pseudo-first-order reaction with power dissipation of 300 W, are found to be $17.7 \times 10^{-3}\ min^{-1}$, $20 \times 10^{-3}\ min^{-1}$, $23 \times 10^{-3}\ min^{-1}$, and 33×10^{-3} min for 28, 40, 50, and 120 kHz, respectively. While, in the case of a conventional approach, the rate constant was found to be $8.5 \times 10^{-3}\ min^{-1}$ [78]. Later, in 2014, the kinetics of the production of 1-butoxy-4-Nitrobenzene under aqueous potassium carbonate was studied and compared in terms of conventional as well as US-assisted approach. Pseudo-first-order kinetics fitted and the reported K_{app} value is $26.72 \times 10^{-3}\ min^{-1}$ under highly intense ultrasonication (40 kHz, 300 W). It is almost fivefold more than that of obtained in the traditional one which is (K_{app} value) $5.12 \times 10^{-3}\ min^{-1}$. The intense blending and increased mass transfer were investigated as the responsible parameters for the enhancement (affecting) in the kinetics [108].

6.2 Homogeneously or heterogeneously catalyzed reactions

The kinetics of methyl butyrate synthesis has been reported and it was found that pseudo-homogeneous model cannot be fitted to the available kinetic data because the criteria of this model do not consider certain aspects such as adsorption at the surface of catalyst. However, Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (ER) models were well correlated with kinetic data and accounted for the reverse reaction. The reported activation energy for homogeneous kinetics was 18.29 kJ/mol and heterogeneous kinetics was in the range of 49.31–57.54 kJ/mol. In the case of homogeneously or heterogeneously catalyzed reactions, both the reactive and productive material is known to be adsorbed on catalyst surface which is an important aspect for validating the model with experimental data [15].

Also, in 2015, the synthesis of fatty acid methyl esters using renewable raw material under ultrasound irradiation was investigated. Its dual-stage approach involves acid esterification of Nagchampa oil under H_2SO_4 further continued by transesterification catalyzed by CaO. Second-order kinetics fitted the data properly, and estimated rate constant for esterification (stage-one) for ultrasound sonication was $2.3 \times 10^{-2}\,\mathrm{L\,mol^{-1}\,min^{-1}}$ and for conventional approach reduced to $0.5 \times 10^{-2}\,\mathrm{L\,mol^{-1}\,min^{-1}}$. Also, in case of the second stage of esterification, $17.1 \times 10^{-2}\,\mathrm{L\,mol^{-1}\,min^{-1}}$ was the rate constant with ultrasound sonication and $0.67 \times 10^{-2}\,\mathrm{L\,mol^{-1}\,min^{-1}}$ was without ultrasound at 50°C. However, at 50°C the second-order rate constant for transesterification enhanced from 16.6×10^{-2} to $25.5 \times 10^{-2}\,\mathrm{L\,mol^{-1}\,min^{-1}}$ after the application of sonication, which was attributed to the enhanced mixing and microscale turbulence (physical effects) [109].

6.3 Enzyme catalyzed reactions

Recently in 2018, kinetics for the synthesis of isobutyl propionate using lipase as a catalyst in the absence of the solvent was reported under acoustic cavitation. The kinetic model was fitted with the help of three mechanisms such as random bi-bi, Ping-Pong bi-bi, and ordered bi-bi. The closest fit was given by Ping-Pong bi-bi model and high value of V_{max} ensured the improved tendency for splitting of lipase-substrate complex to breakdown and get the product. The reported $V_{max} = 50.0\,\mathrm{M\,min^{-1}\,g^{-1}}$ was higher under ultrasound sonication in comparison with the conventional approach, which was 0.5 $\mathrm{M\,min^{-1}\,g^{-1}}$. Also, the enhancement in rate constant ensured the higher tendency for splitting of lipase-substrate complex to get the product [110]. Similarly, for cellulose hydrolysis, an increased value of V_{max} and reduced value of K_m under ultrasonication (at $11.8\,\mathrm{W\,cm^{-2}}$ intensity of power) ensured higher catalytic activity with an enhanced affinity towards the substrate in comparison with conventional approach [111]. V_{max} and K_m values in the case of evaluation of amylase activity over the temperature range of 35–65°C have been investigated. With an increase in temperature, the km value remained constant throughout; on the other hand, V_{max} increased with temperature under ultrasonication. Whereas, the reduction in km value by 65% and enhancement in V_{max} up to 190% has been observed with an increase in temperature in the absence of ultrasonication [112]. The observed changes in the V_{max} value under ultrasound cavitation can be associated with intense pressure, shear force, and temperature of the system. Enzymatic ultrasound irradiation was reported as beneficial in terms of rapid and efficient product formation along with a higher affinity for the substrate [113]. Overall, we can summarize that, even though US-assisted mechanism gives an increased rate of reaction (kinetic rate constants), but in model fitting the class of the reaction should be considered as there is no consistency in the applicability of kinetic models.

7. Industrial applications of US-assisted organic reactions

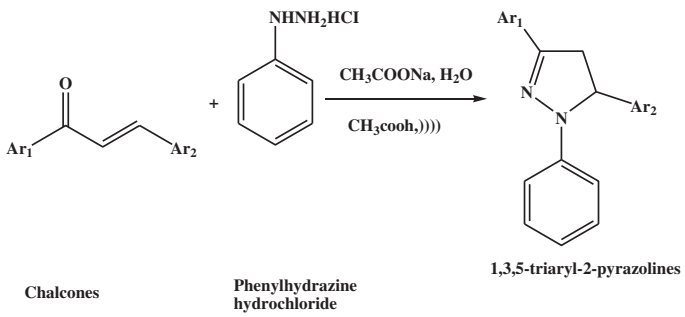
Chemical, pharmaceuticals, food, and bio-technological (production) industries have increased their interest in US-assisted configurations. The reported applications of ultrasound-assisted reactions are in organic synthesis, polymerization, environmental protection (ultrasonography), ultrasonic therapy, medication extraction and synthesis, food packing and equipment, food analysis and inspection, food processing, gene engineering, and enzyme engineering. Hence, applications of US-assisted organic synthesis are described in terms of a variety of chemical reactions, which are divided into different classes.

7.1 Heterocyclic compounds

Heterocyclic compounds are used in the diagnosis of various diseases due to their biological activities. However, they have a tremendous response in pharmaceutical industries, where to fulfill their demand, we cannot be dependent on natural source plant. Therefore, the synthesis of such compounds using different routes is carried out. Along with their biological and industrial applications, they contribute to help any developed human society as well. Also, for human and animal health, a large number of heterocyclic natural products are available with high importance, viz., pesticides, antibiotics, alkaloids, and cardiac glycosides. Hence, many researchers are continuously working on new designs to come out with better pharmaceuticals, pesticides, rodenticides, and weak killers by natural models. Therefore, the requirement of new and effective production processes of new heterocycles is high. Nowadays, researchers are facing a major challenge in the development of environmentally friendly and efficient technologies coupled with green chemistry. Some of the important sonochemical synthesis of heterocycles are given below.

7.1.1 Synthesis of pyrazoline derivatives

In comparison with various pyrazoline derivatives, 2-pyrazolines has been often reported [114, 115]. In order to produce 1,3,5-triaryl-2-pyrazolines, the chalcones reacted with phenylhydrazine hydrochloride under ultrasonication through sodium acetate-acetic

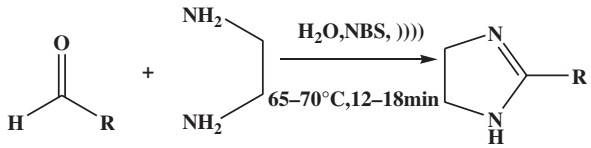


Scheme 15 The reaction of chalcones with phenylhydrazine hydrochloride under ultrasonication to produce 1,3,5-triaryl-2-pyrazolines.

acid aqueous solution for 1.5–2.0 h (Scheme 15) [116]. By employing ultrasound irradiation, it has overcome drawbacks of conventional methods and yielded 1,3,5-triaryl-2-pyrazolines in a shorter time interval and higher yield (83%–96%).

7.1.2 Synthesis of 2-imidazolines

In 2009, it has been reported that the aldehydes reacts with ethylenediamine in the presence of NBS along with an aqueous medium under ultrasound irradiation and gives a series of 16 2-substituted-2-imidazolines (80%–99%) (substituents are R = Ph, Me-4-Ph; MeO-4-Ph; $(MeO)_2$-3,4-Ph; $(MeO)_3$-3,4,5-Ph; Ph-4-O-C(O)-Ph; Cl-4-Ph; Cl-2-Ph; Cl_2-2,4-Ph; NO_2-4-Ph; NO_2-3-Ph; Naphth-2-yl; Fur-2-yl; Benzofur-2-yl; Pyridine-2-yl; Quinolin-2-yl) (Scheme 16) [117].

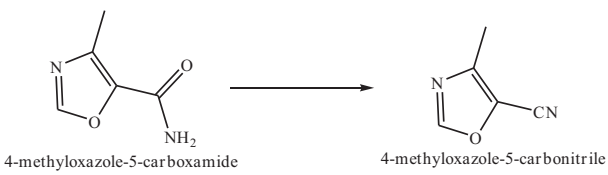


Scheme 16 Synthesis of 2-imidazolines using aldehydes and ethylenediamine in the presence of NBS under ultrasound irradiation.

Also, the very first synthesis of tri-substituted imidazoles using Ionic liquid [EMIM] OAc under ultrasonication has been studied in 2010 [118]. Further, various trends for the synthesis of imidazolines have been reported [119]. It is a greener aspect to use reusable catalyst, aqueous medium, and mild reagents under ultrasound irradiation.

7.1.3 Synthesis of vitamins

Synthesis of 4-methyl-oxazole-5-carbonitrile under the influence of ultrasound has been reported with a 61% yield in a short period time. This compound is acting as a building block in the production of vitamin B6 (Scheme 17) [120]. Furthermore, the ultrasound irradiation for dehydration of other amides has been reported to produce respective nitriles with higher yields in a shorter time.

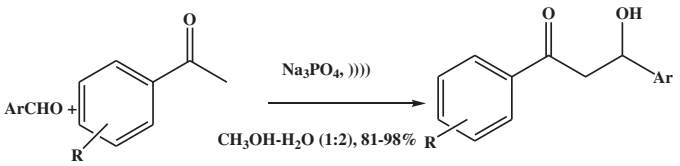


Scheme 17 Formation of 4-methyl-oxazole-5-carbonitrile under the influence of ultrasound irradiation.

7.2 Condensation reactions

7.2.1 Synthesis of β-hydroxyl ketones

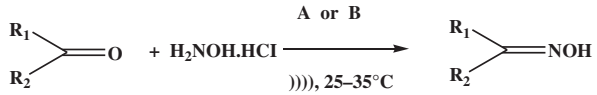
The reaction of aldehydes and substituted acetophenone with (methanol-water) mixed solvent using trisodium phosphate under ultrasonication has been reported. With the concept of cross-aldol condensation, synthesis of hydroxyl ketones resulted in remarkably excellent yield (Scheme 18) [121].



Scheme 18 Cross-aldol condensation of aldehydes and substituted acetophenone using trisodium phosphate under ultrasonic irradiation.

7.2.2 Synthesis of ketoximes

The synthesis of ketoximes has been studied via condensation of ketones with hydroxylamine hydrochloride in ethanol under ultrasonication [122]. Also, oximes (50.7%–98.7%) are synthesized through condensation of aldehydes and ketones along with hydroxylamine hydrochloride in EtOH using highly intensive ultrasonication, which is beneficial in terms of ambient conditions, lesser reaction time, and improved yields as compared with the conventional approach (Scheme 19) [123].

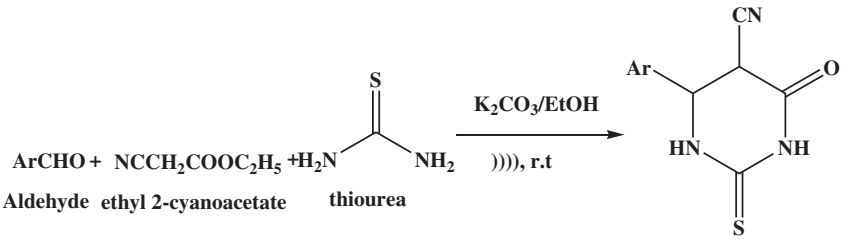


A: Na_2SO_4(1.0 mmol); B: without Na_2SO_4

Scheme 19 Ultrasound-assisted condensation of ketones with hydroxylamine hydrochloride in ethanol.

7.2.3 Synthesis of 4-oxo-2-thioxohexahydropyrimidines

Condensation products (Thiouracil) show pharmacological and inhibitory nature, viz., anti-inflammatory and virucidal activities. Hence, the formation of 4-oxo-2-thioxohexahydropyrimidines has been studied through one-pot condensation of aldehydes, ethyl cyanoacetate along with thiourea in the presence of potassium carbonate as a catalyst in ethanol. Due to the application of ultrasound irradiation, the reaction time was reduced which resulted in completion of the reaction in a single stage. Also, one-pot condensation resulted in an enhanced yield of 20%–90% as compared to conventional two-step method (Scheme 20) [124].

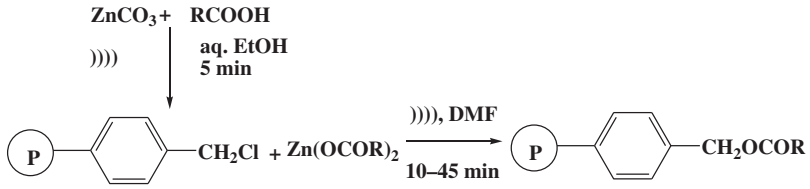


Scheme 20 Ultrasound-assisted one-pot condensation to produce 4-oxo-2-thioxohexahydropyr imidines.

7.3 Substitution reactions

7.3.1 Reaction of carboxylic acids to Merrifield resin

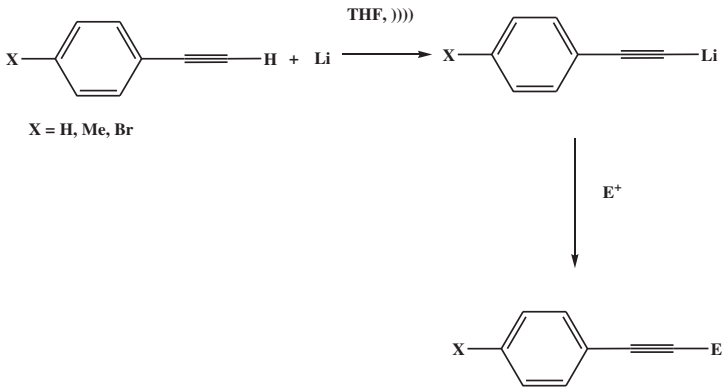
Ultrasonication of the acid in aqueous alcohol reacted with zinc carbonate resulted in zinc salts of carboxylic acids. Furthermore, the zinc salts reacted with chloromethyl polystyrene (Merrifield resin) established anchored benzyl esters under ultrasound irradiation which finds application to control the magnitude of substitution of benzylic chlorine on the resin and in building peptides as well (Scheme 21) [125].



Scheme 21 The reaction of the alcohol with zinc carbonate to form zinc salts of carboxylic acids using ultrasonication.

7.3.2 Synthesis of functionalized arylacetylenes

A convenient and inexpensive route for the synthesis of functionalized arylacetylenes through ultrasonication has been studied in the presence of metallic lithium (Scheme 22) [126].



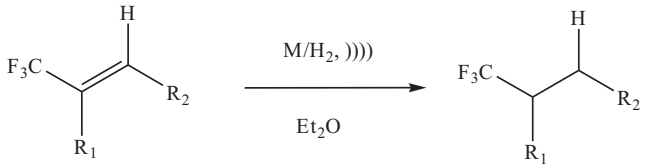
Scheme 22 Formation of functionalized arylacetylenes in the presence of metallic lithium using ultrasonic irradiation.

Ultrasonication has improved the synthesize of arylacetylenes with metallic lithium in the presence of THF by using different types of electrophiles and reported as an efficient, moderate, feasible, and cost-effective route without application of strong bases.

7.4 Reduction reactions

7.4.1 Synthesis of fluorinated alkanes and cycloalkanes

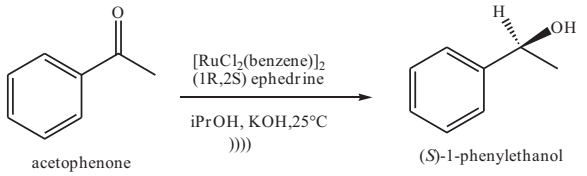
High-intensity ultrasound has been applied to synthesize fluorinated alkanes and cyclohexanes. The reaction is carried out using hydrogenation of sterically hindered and electron-poor perfluoroalkyl alkenes under hydrogen at atmospheric conditions (pressure and temperature) (Scheme 23) [127]. Ultrasound fastened the rate of hydrogenation, and vice versa, i.e., the reduction in the rate of hydrogenation has been reported in the absence of ultrasound. Also, in the hydrogenation of perfluoroalkyl alkenes, the presence of ultrasound for coupling with metallic catalysis enhanced efficiency.



Scheme 23 Production of fluorinated alkanes and cyclohexanes using hydrogenation of perfluoroalkyl alkenes under ultrasonication.

7.4.2 Hydrogenation of ketones

Sonication enhanced the asymmetric transfer hydrogenation of ketones catalyzed by Ru (II)arene/amino alcohol (Scheme 24) [128]. After comparing the reaction which was conducted at 25°C without ultrasound, significant enhancement in rate as well as catalytic activity (5–10 times) without changing the enantioselectivity has been observed.



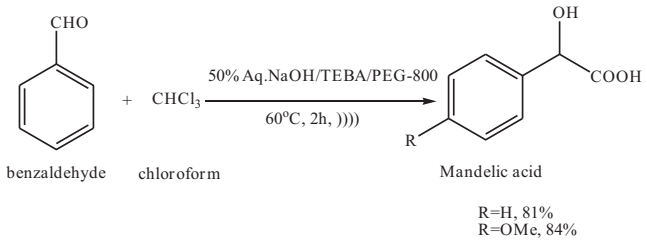
Scheme 24 Ultrasound-assisted hydrogenation of ketones in the presence of Ru(II)arene/amino alcohol.

7.5 Addition reactions

7.5.1 Synthesis of mandelic acid

Mandelic acid, also known as α-hydroxyphenyl acetic acid, which is a racemate, plays a role of principal raw material in the resolution of isomers to obtain (R)-mandelic acid and (S)-mandelic acid. Evaluation of mandelic acid has been carried out in the presence of

ultrasonication by reacting benzaldehyde with chloroform (81% yield, 60°C for 2h) using PTC (triethyl benzyl ammonium chloride (TEBA) and polyethylene glycol-800 (PEG-800) (Scheme 25) [129]. The reaction was reported beneficial in terms of the lesser reaction time and enhanced yield than the classical approach. Also, the formation of mandelic acid by changing PTC to tetrabutyl ammonium bromide (TBAB) reacted with benzaldehyde and chloroform has been reported with the benefits of the lesser reaction time of 2h and enhanced yield of 89.6% [76].

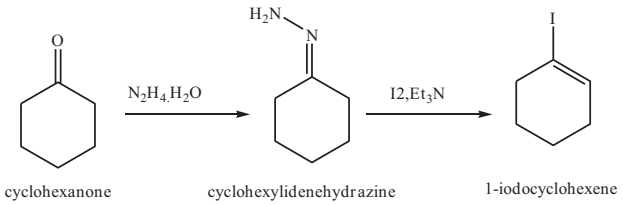


Scheme 25 The reaction of benzaldehyde with chloroform using PTC under ultrasonication to produce mandelic acid.

7.6 Photochemical reactions

7.6.1 Synthesis and photochemistry of 1-iodocyclohexene

The formation of radical has been evaluated under ultrasonication by the substantial decrease of 1-iodocyclohexene in the absence of the zinc (Scheme 26) [130]. An application of ultrasound impacts photo behavior along with its radical route. The reaction under ultrasound was reported advantageous as sonochemical stirring enhanced yield as compared to mechanical stirring as well as along with ultrasound; zinc also contributed to radical and ionic products.



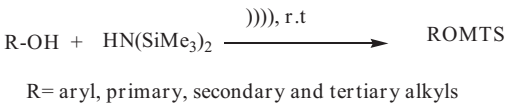
Scheme 26 Formation of 1-iodocyclohexene under ultrasonication using cyclohexanone.

7.7 Protection/deprotection

7.7.1 Protection of alcohols

Due to the application of inorganic and analytical chemistry, protected hydroxyl functionalities became essential intermediates. Formation of a wide range of alcohol and phenols by hexamethyldisilazane at room temperature under the application of highly intensive sonochemistry (ultrasonication) has been reported with excellent yield in the

absence of solvent or any additive (Scheme 27) [131]. Additionally, in the case of protection of hydroxyl groups, good to excellent chemoselectivity was demonstrated along with providing exclusive protection of phenols in the presence of aromatic amines.

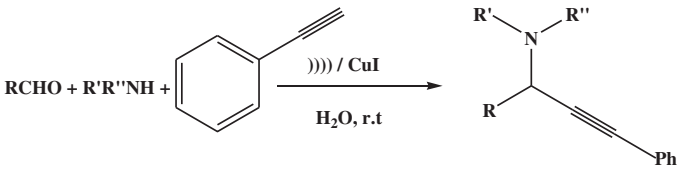


Scheme 27 Synthesis of a wide range of alcohol and phenols by hexamethyldisilazane using ultrasonication.

7.8 Coupling reactions

7.8.1 Synthesis of propargylamines

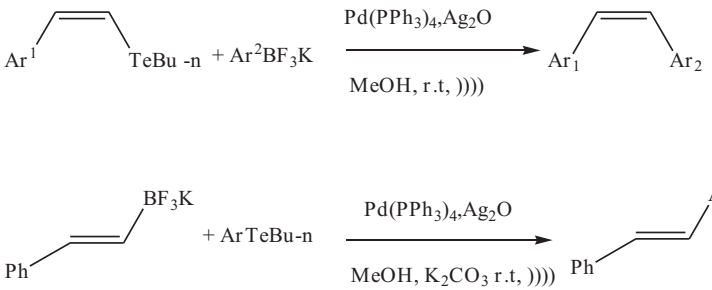
At room temperature, the application of ultrasound irradiation to the addition of metal acetylides to imines resulted in the formation of propargyl amines. Good to excellent yield has been evaluated with copper iodide in aqueous medium at room temperature (Scheme 28) [132]. Ultrasonication encouraged three-component reaction in terms of lesser reaction time as compared to the certain hours required for conventional heating. It is also carried out at an ambient temperature, without the use of any organic solvents, and water is the only by-product, making the process eco-friendly.



Scheme 28 Formation of propargyl amines by addition of metal acetylides to imines in presence of ultrasonication.

7.8.2 Synthesis of Z and E stilbenes

Potassium aryl cross-coupled with vinyltrifluoroborate salts, aryl, and vinylic tellurides by using Palladium (0) as a catalyst has been reported. Coupling resulted in the synthesis of stilbenes with very good to excellent yield. Also, it has the ability to make Stilbenes with a variety of functional groups (Scheme 29) [133]. The combined benefit of using potassium



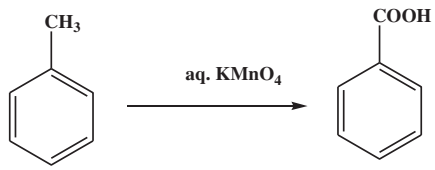
Scheme 29 Formation of Z and E stilbenes using cross-coupling reaction under ultrasonic irradiation.

organotrifluoroborate salts with ultrasonication provides Suzuki coupling faster and attractive than the conventional method because of tolerance (indulgence) of functional groups in both substrates. Also, the Suzuki coupling is more chemoselective, and aryl tellurides are reported as highly reactive than aryl halides.

7.9 Oxidation reactions

7.9.1 Oxidation of alkylarenes to the corresponding acids

Toluene oxidation with the help of aqueous potassium permanganate using heterogeneous catalyst under acoustic as well as hydrodynamic cavitation has been reported. Factors like the weight of potassium permanganate, toluene to aqueous phase ratio, time, orifice plate, and pump discharge pressure have been investigated. Also, acoustic cavitation compared with hydrodynamic cavitation in terms of moles of product formed after the supply of 1 kJ of energy, was stated as 4.63×10^6 mol of product formed under hydrodynamic cavitation whereas 2.70×10^5 mol in acoustic cavitation [134]. Therefore the application of hydrodynamic cavitation in the oxidation of toluene provided with sixfold better product yield, energy-efficient and mild reaction conditions as compared to acoustic cavitation (Scheme 30).

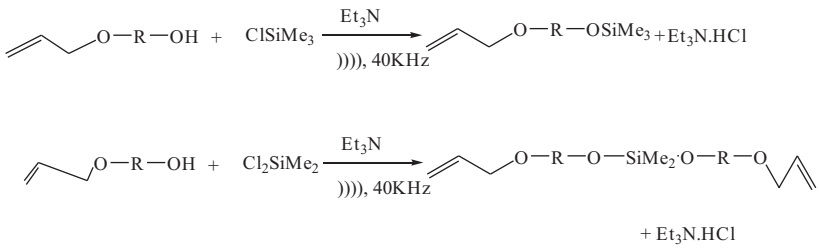


Scheme 30 Oxidation of toluene in presence aqueous potassium permanganate to produce carboxylic acid under hydrodynamic cavitation.

7.10 Polymerization reactions

7.10.1 Synthesis siloxane monomers

The reactions of homoallyloxyalcohols and chlorosilanes under the influence of ultrasonication has been reported for the formation of allyl ether functionalized siloxanes. The cationic UV-curable allyl ether functionalized siloxane monomers type 1 $CH_2{=}CH\text{-}CH_2\text{-}O\text{-}RO\text{-}Si(CH_3)_3$ and type 2 $CH_2{=}CH\text{-}CH_2\text{-}O\text{-}R\text{-}O\text{-}Si(CH_3)_2\text{-}O\text{-}R\text{-}CH_2\text{-}CH{=}CH_2$ have been synthesized at room temperature with the highest yield in less time and without a catalyst. Employed ultrasonication results in faster reaction along with the enhanced reaction rate which has been described in terms of vigorous stirring of liquid and the energy required for mechanical and chemical effects. Also, siloxane is used in radiation curing applications as they combine thermal, chemical, or physical properties of siloxanes and allyl ethers. With the application of transition metal complexes as a catalyst (ruthenium), allyl ethers isomerize with 1-propenyl ether (Scheme 31) [135]

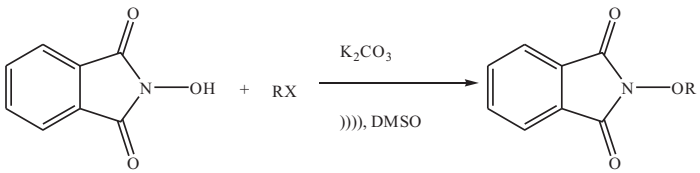


Scheme 31 Synthesis of siloxanes by reacting homoallyloxyalcohols with chlorosilanes using ultrasonic irradiation.

7.11 Alkylation and acylation reactions

7.11.1 Synthesis of N*-alkoxyphthalimides*

In preparation of alkoxyamines, *N*-alkoxyphthalimide derivatives act as a prime synthetic intermediates. With the application of ultrasonication, it accelerates the rate of formation of *N*-alkoxyphthalimides by alkylation of *N*-hydroxyphthalimide with alkyl halides using potassium carbonate as a catalyst with 64%–99% yield in DMSO in reduced reaction time of 0.7 h (Scheme 32) [136]. Also, ultrasonication maintains moderate conditions such as 25–35°C for alkylation of *N*-hydroxyphthalimide with alkyl halides.



Scheme 32 Alkylation of *N*-hydroxyphthalimide with alkyl halides to produce *N*-alkoxyphthalimides in the presence of ultrasound irradiation.

8. Conclusion and future aspects

In a comparison with conventional methodology, US-assisted organic synthesis is considered a greener approach which results in remarkable advantages such as shorter reaction time as well as enhanced yields. Water, ionic liquids, etc. are used as replacements for volatile and toxic organic solvents. The use of inexpensive, efficient, or reusable catalysts is the developments achieved using high-intensity ultrasound irradiation. Based on the application of sonochemistry in organic synthesis, less waste accumulation, operation safety, increased productivity along with less material and energy consumption are the greener aspects achieved. Also, the estimated cost for the targeted process can be lowered by optimizing different operational and geometric parameters. The factors such as power, duty cycle, frequency, agitation speed are valuable to intensify the process. Thus, the

application of optimum power is preferable depending on operation condition and reactor configuration. Lower frequencies are used in the case of systems where physical effects are mandatory because of mass transfer conditions. Also, high frequencies are favored for those operations where involvement of intrinsic kinetics or free radical mechanisms are used to limit the chemical reactions. In the case of enzymatic reactions, the duty cycle, agitation speed, and operating temperature need to be optimized because conversion reduces well below optimum value as a result of deactivation of enzymes.

Additionally, for large-scale operations designing of the reactors would be critical. The multiple transducer type configurations are recommended for commercial operations. It is summarized that ultrasound sonochemistry is an outstanding approach at the laboratory level and in the future, it needs to be synthetically elaborated as a greener alternative for industrial applications.

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CHAPTER 2

Sonochemical protocol for catalyst-free organic synthesis

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1. Introduction

With the developing accomplishments of the industries based on synthetic chemistry and research taking place in this area, there is the simultaneous intensification of the issues related to environment and human health [1]. Further, the increase in the issues related to chemical waste, its disposal, and its after-effect especially from chemical industries has inspired the scientists to explore the alternative routes which strictly follow the stringent regulations as per the green chemistry. On the other hand, to achieve sustainable development and to fulfill the collective objective of economical, social, and environmental progress, the chemical industries have a focus in the past few decades to develop the environment-friendly methodologies efficiently so as to reduce the overall generation of waste by following the principles of green chemistry.

The evolution of the green chemistry took place as a result of the Pollution Prevention Act of 1990 in United States conferring the elimination of pollution through proper modifications in the synthetic protocol instead of remedy and management at disposal level [2]. This branch of chemistry is the set of 12 basic principles which ensures either the reduction or the removal of harmful chemicals in the synthetic design [3]. In this context, a skillful and a rational transformation in synthetic chemistry has been observed in the last few decades. Nonetheless, the one component that plays a vital role in the design of a chemical reaction is the use of catalyst which not only enhances the feasibility but also the selectivity of the reaction [4]. However, it has been found that the extensive use of expensive and hazardous catalysts is not only harmful but also adds to the cost of the synthetic process. Keeping in view the criteria of the green chemistry, researchers are making pervasive efforts to decrease the harmful aspects of the catalytic systems via some suitable alternatives but the best way-out is to design a protocol which would be equally efficient without the use of catalytic resource [5]. Sonochemistry is seen as one of the few alternatives that can be used as a powerful resource for organic synthesis with improved efficiency and the least generation of waste by avoiding the use of toxic and hazardous reagents and chemicals [6].

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Sonochemistry technique is able to activate the reaction with the added benefits of better yields, speed, and mild reaction conditions by using cost-effective equipment [7].

The use of ultrasonics in chemistry which involves the use of safe acoustic radiations [8] falls into the category of green chemistry and hence ultrasound-promoted reactions are recognized to be one of the most favorable protocols for the organic synthesis. This method is associated with the phenomenon of acoustic cavitation which involves the bursting of the bubbles generating a highly elevated temperature and pressure in the limited region known as hot spots that reduce the time span, increases yield, and minimizes the release of waste [9].

The roots of the sonochemistry can be traced at the beginning of the 19th century when in 1917, Langevin developed "Echo Sounding Technique" for the estimation of the approximate depth of the water followed by the introduction of the mechanical application of the power ultrasonics in emulsification [10]. But the use of ultrasonics in the chemical activation started in 1927 after Wood and Loomis reported the impact of the power ultrasound with high intensity on the chemical, physical, and biological structures [11]. Later in 1986, the International Symposium on sonochemistry was organized by the Royal Society of Chemistry at Warwick University, UK, as a part of their Autumn Meetings, which eventually accentuated the use of ultrasonics in the chemistry [12]. Afterward, a great advancement was seen in the development of sonochemistry especially toward the development of ultrasound-assisted catalyst-free protocols which was shown by several publications and the review articles [13].

2. Acoustic cavitation

The term "Acoustic cavitation" can be defined as the growth, compression, and subsequent collapse of the liquid bubbles because of the incident high-intensity ultrasonic radiations [14] and serve as the efficient means of concentrating the scattered energy of sound. While describing the calculative model of the bursting bubbles, Rayleigh in 1917 reported the formation of high temperature and high pressure in the microenvironment of the bubble. After a decade in 1927, Richards and Loomis were the first to report the biological and chemical changes introduced under the influence of the acoustic field [15, 16].

Studies have revealed that when the amplitude of the pressure wave of the acoustic field becomes greater than 0.5 MPa, the turbulence introduced leads to the increase in the size of the nucleation site thus forming cavity of bigger dimensions, which in general, is filled with the gas vapors. Intrinsically, the bubbles of this kind are highly unstable which finally gets collapsed with the liberation of an enormous amount of energy [17]. It has also been found that the process involving bursting of bubbles is nearly adiabatic [18] and sets up a temperature of thousands of degrees known as hot spots within the small neighborhood of the bubble thereby creating drastic turbulence. This heightened energy then adds to the inherent energy of the organic molecules in order to meet the required activation

energy for the major fraction of the organic compounds thereby resulting in their mass transfer and hence decrease the reaction time along with considerable improvement in yields [19]. Many times, this phenomenon can even result in the organic synthesis without any added catalyst. Therefore, this sonochemical approach can aid chemists in devising the catalyst-free protocol for organic synthesis (Fig. 1).

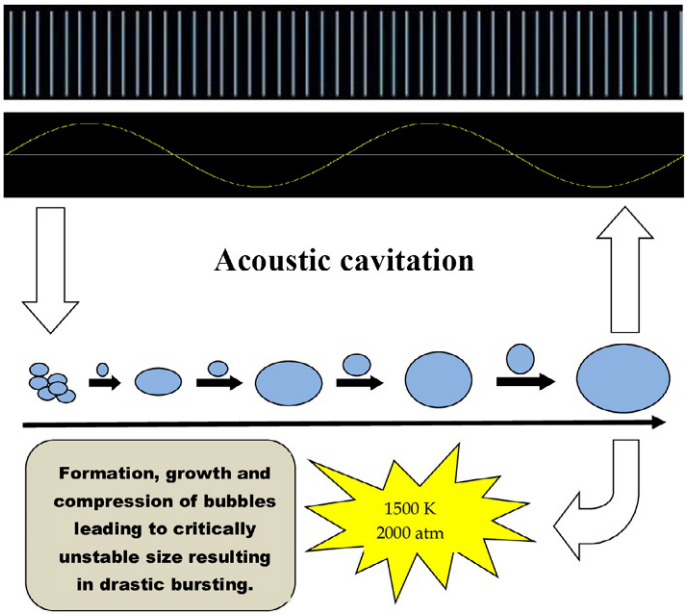


Fig. 1 Representation of basic phenomenon of acoustic cavitation.

3. Equipment requirement for sonochemical reactions in laboratory

In order to carry out any sonochemical reaction either on a laboratory scale or on a commercial scale, the primary requirement is to install a source of ultrasound waves. In general, the ultrasonic waves are generated by the use of the transducers which are commonly employed with the piezoelectric material capable of converting the electric power to the mechanical power in the form of sound waves [20]. In addition to this, one can also make use of the phenomenon known as magnetostriction based on the changing dimensions of the metals. In this process, the metals like Ni, Fe, etc. are magnetized to bring the change in their dimensions that ultimately lead to the production of sound waves. Also, the whistle or siren generators are available for the production of the requisite energy source. In the majority of the applications, the most common ultrasound source is the transducer which comprises of piezoelectric material held on metallic support forming a "piezoelectric-sandwich"-type setup [21].

As far as the laboratories are concerned, the two commonplace resources of ultrasound are the ultrasonic cleaning bathtub [22] and the ultrasonic horn system [23].

3.1 The ultrasonic cleaning bathtub

For laboratory applications, the ultrasonic cleaning bathtub is the most conventional and the most economic source of ultrasonic waves. This equipment is quite handy in usage as it directly involves the immersion of the reaction vessel into the bathtub allowing the uniform distribution of the energy into the reaction atmosphere in an inert atmosphere. Even though the cleaning bathtub can also be used in place of the reaction vessel, but the issues related to the corrosion and the vapors, gases involved refrain its direct application. No major alterations are needed in this equipment but it does require a thermostatic manager for maintaining the temperature of the reaction vessel (Fig. 2).

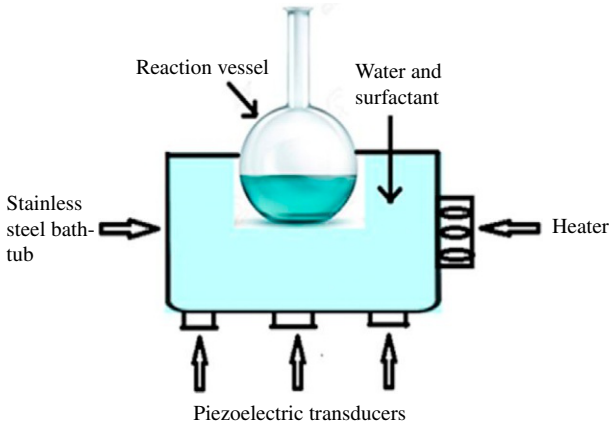


Fig. 2 Ultrasonic cleaning bathtub for sonication.

3.2 Ultrasonic horn system

The other resource that can be employed for the generation of the ultrasonic waves is the ultrasonic horn system. Instead of transferring energy from the equipment to the reaction vessel through some medium or a water tank, this system allows us to transfer the acoustic energy required directly to the reaction vessel. This source of ultrasonic is costlier than the conventional bathtub equipment and also requires the special skills for usage as it involves the use of special seals in order to carry out the reaction (Fig. 3).

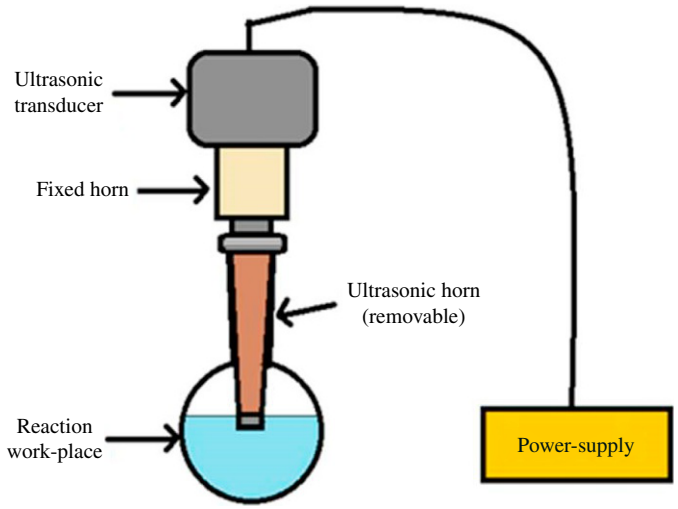


Fig. 3 Ultrasonic horn system for sonication.

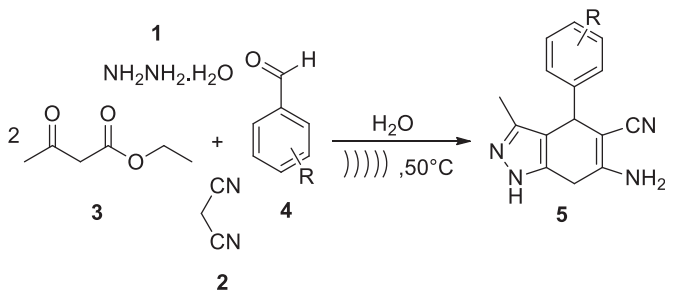
4. Application of ultrasound in catalyst-free organic synthesis

With the increasing interest toward the modification or improvement of the conventional synthetic methodologies and prolonged widespread awareness of the safety of the environment along with sustainable development, ultrasonic-assisted catalyst-free synthesis has emerged as the modern and highly innovative alternatives to the traditional catalytic synthetic processes. Since the discovery of the ultrasound as a green and efficient energy source, many attempts have been made by researchers in the past few years to find safer alternatives to the conventional synthetic procedures based on catalytic-free methodologies. In this chapter, we have compiled the sonochemically promoted catalyst-free protocols for the synthesis of biologically relevant molecules.

4.1 Catalyst-free sonochemical synthesis of heterocyclic organic scaffolds

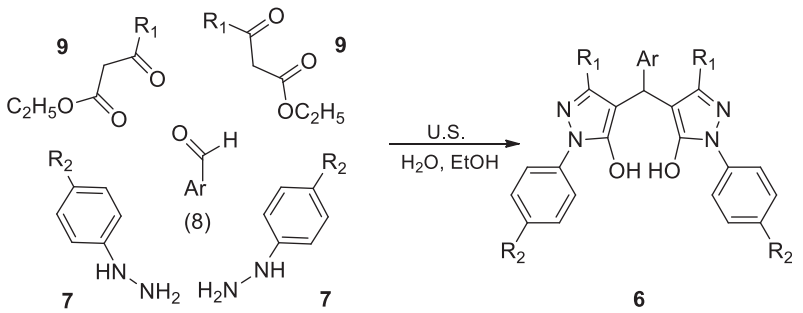
4.1.1 Synthesis of pyrazole-based heterocycles

Pyrazoles are among the spectacular class of heterocyclic scaffolds owing to their diverse biological activities [24, 25]. Thus, the development of new methodologies for the synthesis of this moiety has received considerable attention in the literature. Conversely, most of the available methods are plagued with drawbacks such as low yield, less selectivity, use of hazardous and toxic reagents and/or catalysts, the requirement of elevated temperature. In this context, Shabalala et al. reported an ultrasound-assisted catalyst-free synthesis of the title compound **(5)** through the one-pot multicomponent reaction of hydrazine hydrate **(1)**, malononitrile **(2)**, ethyl acetoacetate **(3)**, and aromatic aldehydes **(4)** as shown in Scheme 1 [26].



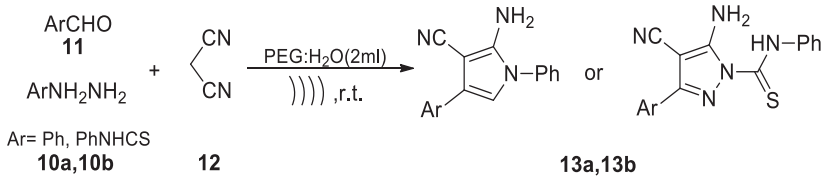
Scheme 1 Synthesis of pyrazoles via catalyst-free ultrasound-promoted multicomponent approach.

Hasaninejad and his coworkers have synthesized a new family of pyrazole-based bioactive heterocycles, 4,4-(arylmethylene)*bis*(3-methyl-1-phenyl-1*H*-pyrazol-5-ols) **(6)** using sonochemical catalyst-free activation through pseudo-five-component route [27]. In this strategy, diversely substituted phenylhydrazine derivatives **(7)**, aromatic aldehydes **(8)**, and ethyl acetoacetate **(9)** were reacted in water/ethanol using ultrasonic irradiation (Scheme 2). The method is not only safe and environmentally benign but also has the advantages of short-reaction times and improved yields.



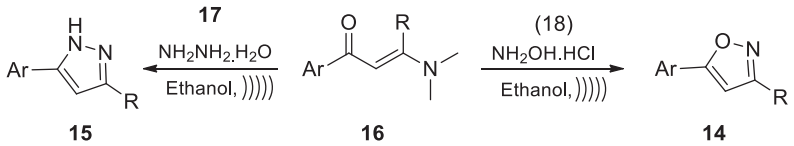
Scheme 2 Sonochemical protocol for the synthesis of 4,4-(arylmethylene)*bis*(3-methyl-1-phenyl-1*H*-pyrazol-5-ols).

Nemati and coworkers have developed an efficient, environment-friendly, cost-effective, and catalyst-free strategy for the synthesis of a diverse range of pyrazoles. In this ultrasound-assisted approach (Scheme 3) [28], 4-phenyl thiosemicarbazide **(10a, 10b)**, aryl-aldehyde **(11)**, and malononitrile **(12)** were reacted in PEG:H_2O at ambient temperature to afford the desired family of pyrazoles **(13a, 13b)**.



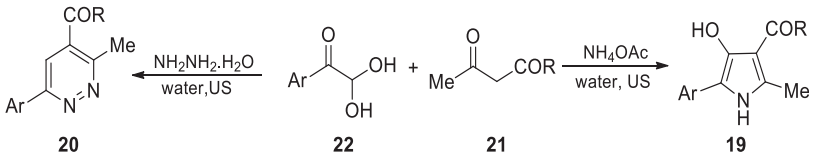
Scheme 3 Synthesis of multi-substituted pyrazoles.

Attributing to the wide spectrum of the biological activities exhibited by isoxazoles **(14)** [29] and pyrazoles **(15)** [30], these two nitrogen-containing heterocyclic compounds have received significant attention from medicinal and synthetic chemists. On account of this, Huang et al. reported the ultrasound-assisted synthesis of series of these biologically attractive targets via condensation of 3-(dimethylamino)-1-arylprop-2-en-1-one **(16)** and hydrazine hydrate **(17)** or hydroxylamine hydrochloride **(18)** in ethanol without involving any catalytic system (Scheme 4) [31].



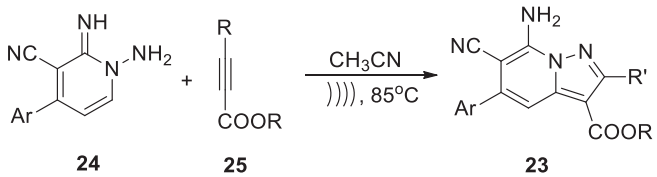
Scheme 4 Catalyst-free sonochemical synthesis of pyrazoles and isoxazoles.

Eftekhari-Sis and Vahdati-Khajeh reported a straightforward, efficient, catalyst-free sonochemical protocol for the synthesis of 5-aryl-4-hydroxy-2-methyl-1*H*-pyrrol-3-carboxylates **(19)** and 6-(4-aryl)-3-methylpyridazine-4-carboxylates **(20)** from the reaction of β-dicarbonyl compounds **(21)** and suitable arylglyoxal hydrates **(22)** in the presence of water (Scheme 5) [32]. Notably, pyrroles and pyridazines are privileged structures known to possess innumerable biological activities [33–36].



Scheme 5 Synthesis of pyrroles and pyridazines using ultrasonic technique.

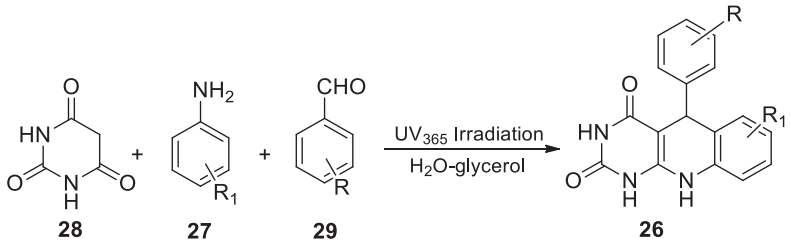
Recently in 2019, Ibrahim et al. reported the facile, one-pot, sonochemically irradiated approach for the synthesis of a novel family of polysubstituted pyrazolo[1,5-*a*] pyridines **(23)** [37]. This methodology involved the [3 + 2] cycloaddition reaction of various derivatives of 1-amino-2(1*H*)-pyridine-2-imine **(24)** and dialkyl acetylenedicarboxylate/alkenyl **(25)** in acetonitrile with no catalyst under ultrasonic irradiation (Scheme 6). In comparison to the conventional methods, this methodology resulted into the synthesis of the novel series with increased regioselectivity and better yields.



Scheme 6 Synthesis of pyrazolo[1,5-*a*]pyridines using sonication.

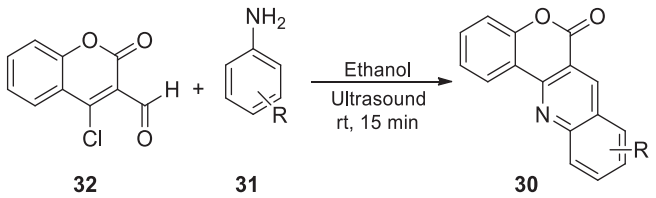
4.1.2 Synthesis of quinoline-based heterocycles

Quinolines and its derivatives have received significant attention in medical research as these are the important units present in the biologically active natural and synthetic molecules [38]. In view of these valid reasons, Nongthombam et al. demonstrated a green, efficient and eco-friendly approach toward the synthesis of series of pyrimido [4,5-*b*]quinoline-2,4-diones **(26)** via ultrasonication of aromatic amines **(27)**, barbituric acid **(28)**, and aryl aldehyde **(29)** at room temperature in water-glycerol medium (Scheme 7) [39].



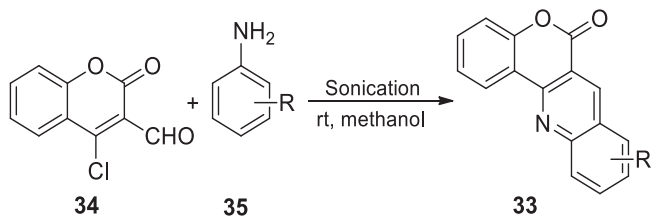
Scheme 7 Sonochemical catalyst-free synthesis of pyrimido[4,5-*b*]quinoline-2,4-diones.

Prasad et al. introduced a one-pot, rapid, convenient, and well-planned approach for the synthesis of fused chromeno-quinoline derivatives **(30).** In this protocol, diversely substituted anilines (**31**) were condensed with 4-chloro-3-formylcoumarin **(32)** under sonochemical conditions in ethanol at room temperature to form chromeno[4,3-*b*] quinolin-6-ones (Scheme 8) [40].



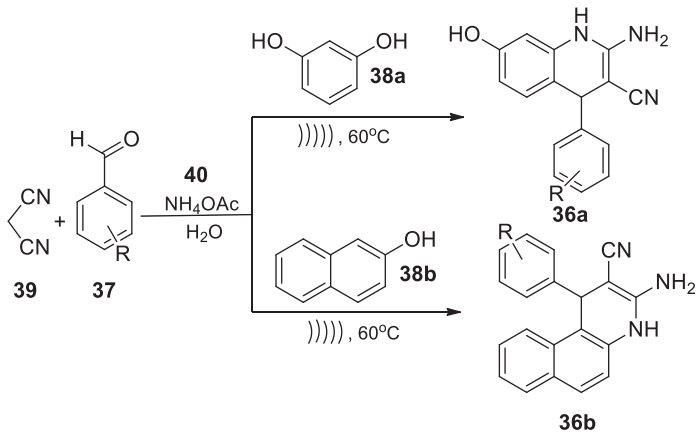
Scheme 8 Green synthesis of chromeno[4,3-*b*]quinolin-6-ones.

On account of the biological efficacies exhibited by the quinolines [41] and the coumarins [42], Mulakayala et al. have successfully synthesized the therapeutically promising series of 6*H*-1-benzopyrano[4,3-*b*]quinolin-6-one **(33)** using sonication under catalyst-free conditions. In this protocol, 4-chloro-2-oxo-2*H*-chromene-3-carbaldehyde **(34)** is treated with a range of aromatic amines **(35)** in methanol at room temperature to deliver the desired product in excellent yields (Scheme 9) [43]. The resultant compounds were further explored for their bioactivity and were found to possess potent anticancer agents.



Scheme 9 Synthesis of quinoline-based potent anticancer molecules.

1,4-Dihydroquinolines and their derivatives are valuable heterocycles and exhibit a variety of biological activities such as antihypertension [44], antiallergic [45], anti-inflammatory [46], etc. The majority of the traditional methods available for the synthesis of these molecules are plagued with the drawbacks of the long reaction times, less reaction yield, and the stringent reaction conditions. Pagadala and coworkers demonstrated an improved procedure by utilizing ultrasonic irradiation technique for the synthesis of different series of these molecules **(36a,36b)** through catalyst-free four-component reaction of aldehyde **(37)**, resorcinol **(38a)**/β-naphthol **(38b)**, malononitrile **(39)**, and ammonium acetate **(40)** in good yield (Scheme 10) [47].

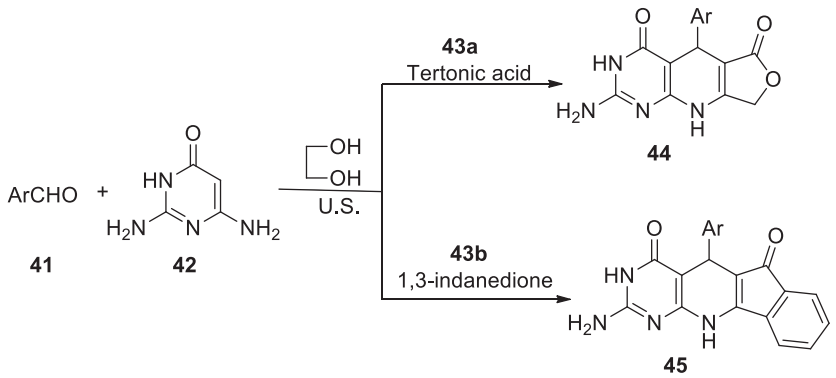


Scheme 10 Ultrasound-promoted four-component catalyst-free synthesis of dihydroquinoline.

4.1.3 Synthesis of pyrimidine-based heterocycles

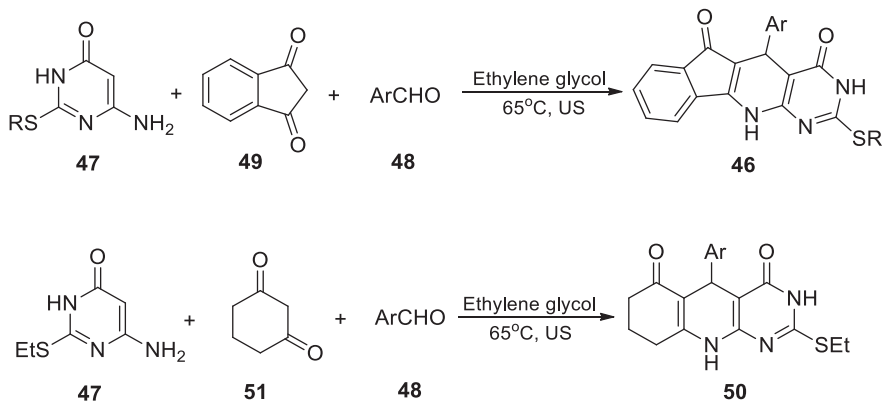
Pyrimidines and their derivatives are one of the significant components of the biologically active compounds [48, 49], making it desirable to develop the mild, convergent and modular approach for their synthesis. The majority of the synthetic pathways are available for the synthesis of this class of azaheterocycles [50]. Typically, the synthesis requires harmful chemicals and stringent reaction conditions. In contrast to it, ultrasonication can be used as a green and sustainable protocol.

Tu et al. described a well-thought, catalyst-free, green protocol for the synthesis of a family of pyrido[2,3-d]pyrimidines. In this protocol, suitably substitued aldehydes **(41)**, 2,6-diaminopyrimidine-4(3*H*)-one **(42)**, and tetronic acid/1,3-indanedione **(43a,43b)** are reacted in the presence of ultrasound irradiation in ethylene glycol as a solvent to deliver the diverse range of pyrido[2,3-*d*]pyrimidines **(44,45)** (Scheme 11) [51].



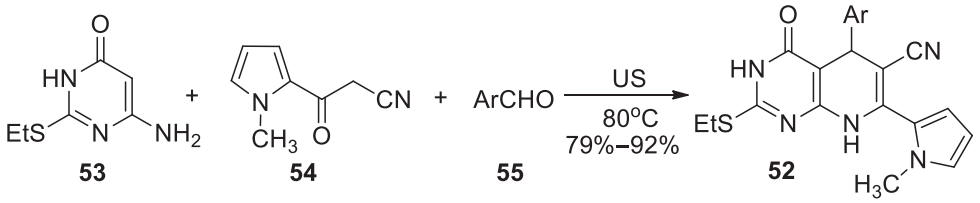
Scheme 11 Sonochemical catalyst-free synthesis series of pyrido[2,3-*d*]pyrimidine.

Mamaghani et al. reported the ultrasonically assisted, environment-friendly, multicomponent protocol (Scheme 12) [52] for the construction of series of biologically significant pyrimidines in a catalyst-free medium. In this method, various derivatives of indenopyrido[2,3-*d*]pyrimidine **(46)** were synthesized through the reaction of 6-amino-2-(alkylthio)-pyrimidin-4(3*H*)one **(47)**, aryl aldehyde **(48),** and 1,3-indanedione **(49)**. The method was successfully extended for the synthesis of an entirely different family of fused pyrimidines **(50)** using cyclohexanedione **(51)** in place of 1,3-indanedione **(49)** as reaction partner.



Scheme 12 Ultrasonically irradiated synthesis of novel pyrimidines.

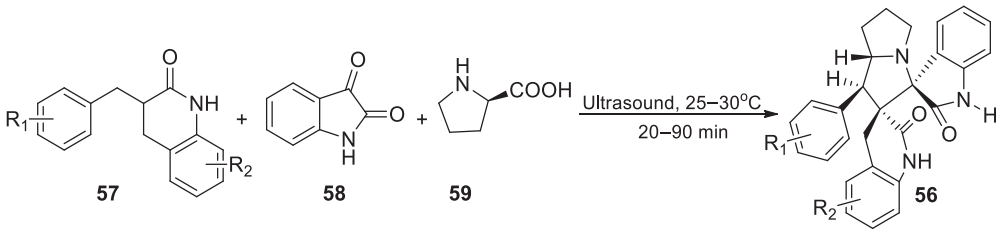
On the other hand, Barghi-Lish et al. also reported ultrasound-assisted catalyst-free simple, efficient, a highly productive protocol for the synthesis of biologically important novel family of pyrido[2,3-*d*]pyrimidines **(52)** (Scheme 13) [53]. This one-pot, three-component reaction involving 6-amino-(ethylthio) pyrimidine-4(3*H*)-one **(53)**, 3-(1-methyl-1*H*-pyrrol-2-yl)-3-oxopropanenitrile **(54)**, and aryl aldehyde **(55)** proceeded at 80°C in ethylene glycol to afford the desired products in excellent yields. Further, it is worth mentioning that the aldehydes bearing electron-withdrawing substituents were found to give better yields.



Scheme 13 Sonochemical catalyst-free synthesis of novel Pyrido[2,3-*d*]Pyrimidines.

4.1.4 Synthesis of spiro-based heterocycles

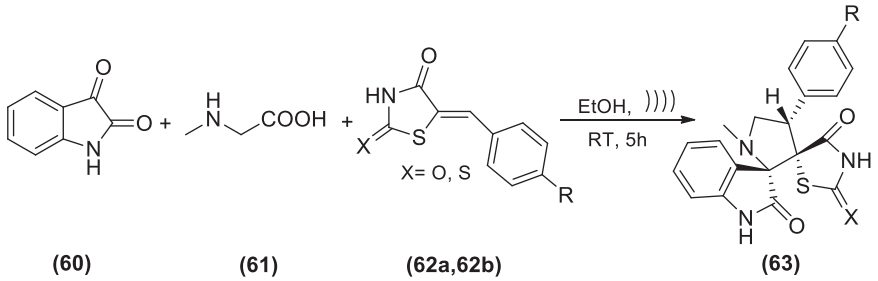
Pyrrolizidines constitute the important class of alkaloids and are widely distributed in natural products [54]. They are known to exhibit the remarkable biological properties and thus there are several synthetic routes available in the literature for their synthesis. In this context, Ge et al. in 2009 employed the ultrasonication technique for the synthesis of a novel series of tetracyclic spiro-based frameworks **(56)** in reduced reaction times and better yields. In this method, Baylis-Hillman amines were made to undergo aza-Claisen rearrangement forming dipolarophile **(57)** followed by 1,3-cycloaddition with reactive azomethine ylide resulted from the interaction of isatin **(58)** and L-proline **(59)** (Scheme 14) [55].



Scheme 14 Ultrasonicated synthesis of dispirocyclic system via Aza-Claisen rearrangements.

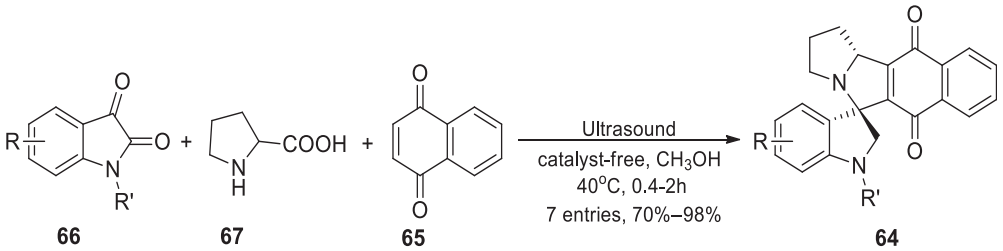
Liu et al. reported the green synthesis of a pharmaceutically significant class of dispiropyrrolidine. In this multicomponent approach, condensation of isatin **(60)**, 2-(methylamino)acetic acid **(61)**, and 5-arylidene-1,3-thiazolidine-2,4-dione **(62a)** or 5-arylidene-4-thioxo-1,3-thiazolidine-2-one **(62b)** under ultrasonication generated

dispiropyrrolidine **(63)** in excellent yields (Scheme 15) [56]. In comparison to the conventional synthetic strategies, this ultrasonic technique resulted in better yields with reduced reaction time.



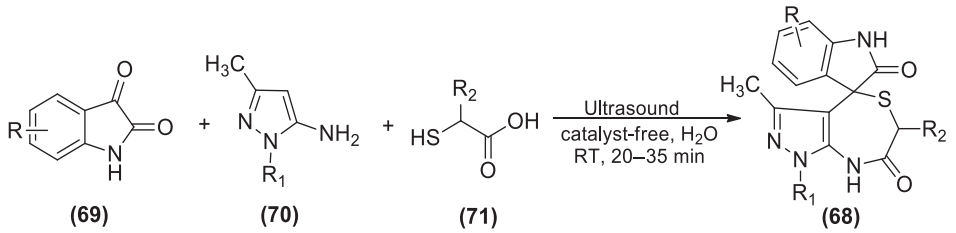
Scheme 15 Domino approach synthesizing derivatives of dispiropyrrolidine via ultrasonication.

In 2012, Chen et al. devised a novel, fast, and productive methodology for the synthesis of therapeutically significant derivatives of spirooxindolepyrrololine **(64)**. This one-pot, multicomponent strategy involves 1,3-dipolar cycloaddition of 1,4-naphthoquinone **(65)**, isatins **(66)**, and diversely substituted α-amino acids **(67)** (Scheme 16). The reaction proceeds through the formation of the reactive azomethine ylide resulted from the reaction of α-amino acids and isatins, which further reacts with 1,4-naphthoquinone in the presence of sonochemical irradiation to afford the desired derivatives in moderate to excellent yields [57].



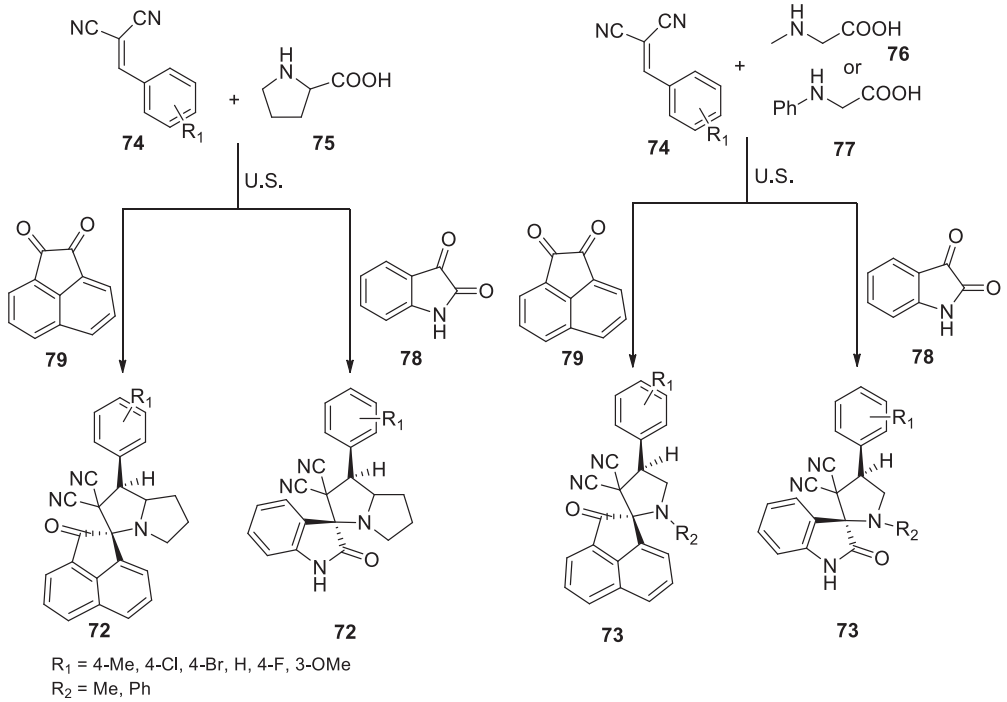
Scheme 16 Sonochemical catalyst-free protocol for the synthesis of spirooxindolepyrrololine.

A well-planned, novel, highly selective, green methodology for the synthesis of pharmaceutically important derivatives of spiro[indole-3,4′-pyrazolo[3,4-*e*][1,4]thiazepines] **(68)** via sonication was demonstrated by Dandia et al. [58]. This catalyst-free multicomponent domino approach utilizing isatin **(69)** along with 3-methylpyrazole **(70)** and α-mercaptocarboxylic acid **(71)** in water in ultrasonic environment resulted into the generation of the required series of bioactive compounds in good to excellent yields (Scheme 17). The structure of the resultant compounds was characterized by a single crystal X-ray analysis.



Scheme 17 Sonochemically irradiated synthesis of spiro[indole-3,4′-pyrazolo[3,4-*e*][1,4]thiazepines].

Rezaei et al. introduced the synthesis of the novel dicyano functionalized derivatives of spiropyrrolizidines **(72)** and spiropyrrolidines **(73)** by the reaction of knoevenagel adducts **(74)**, α-amino acids **(75,76,77)**, and isatin **(78)**/acenaphthenequinone **(79)** in methanol at room temperature. Subsequently, the sonochemical irradiation of the resultant mixture at 25–30°C (Scheme 18) resulted in the synthesis of the novel series of compounds in good to excellent yields [59].

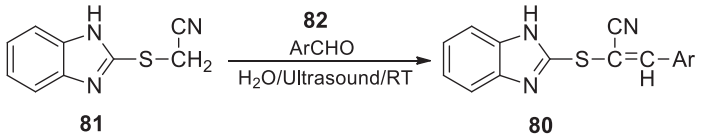


Scheme 18 Ultrasonically mediated synthesis of spiropyrrolidines and spiropyrrolizidines.

4.1.5 Synthesis of bioactive organic compounds bearing nitrile functionality

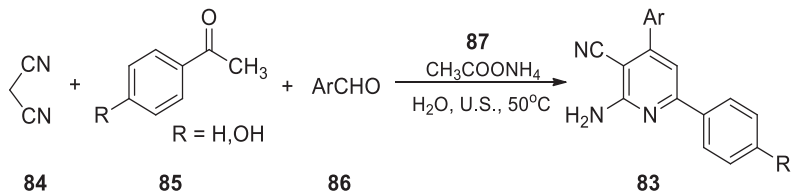
Unsaturated nitriles act as the significant moiety in the skeleton of the various therapeutic drugs and thus intrigue the medicinal chemists to make efforts to synthesize their bioactive derivatives [60]. Rao et al. introduced the sonochemical synthesis of

benzimidazolylthiounsaturatednitriles **(80)** by reacting 2-cyanothiomethylbenzimidazole **(81)** with aromatic aldehydes **(82)** in water at room temperature to afford the requisite product (Scheme 19) [61].



Scheme 19 Sonochemically promoted green synthesis of benzimidazolylthiounsaturatednitriles.

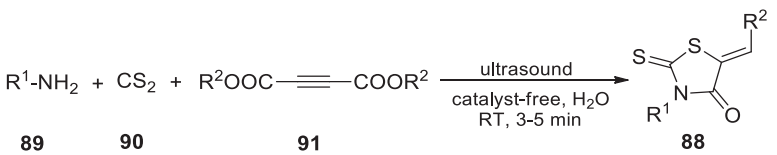
A simple, rapid, environmental-benign, one-pot multicomponent protocol synthesizing 2-amino-4,6-diphenylnicotinonitriles **(83)** via condensing malononitrile **(84),** acetophenone **(85)**, aromatic aldehyde **(86)**, and ammonium acetate **(87)** in sonochemical environment in water at 50°C was reported by Safari et al. [62] (Scheme 20). In contrast to the conventional strategies, this protocol used mild reaction conditions afforded the resultant compounds in better yields without using any catalyst.



Scheme 20 One-pot three-component synthesis of 2-amino-4,6-diphenylnicotinonitriles**.**

4.1.6 Synthesis of rhodanines

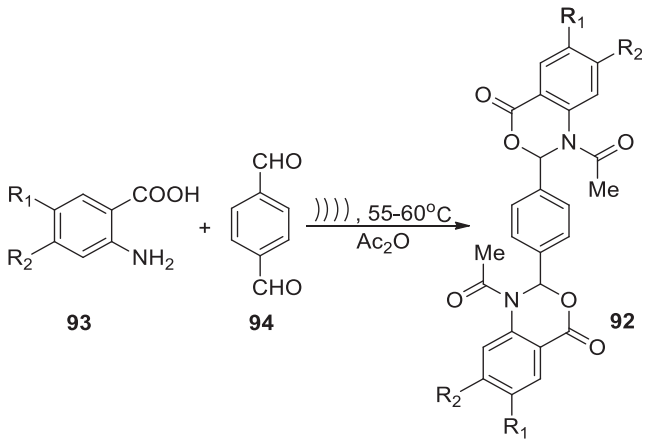
Rhodanine, a five-membered heterocyclic compound holding thiazolidine as a core nucleus is known to exhibit various bioactivities, the most important of which is the inhibition of the β-Lactamase and HCV NS3 protease [63]. In 2011, Rostamnia and Lamei reported a simple, well-planned, and a highly productive methodology synthesizing the rhodanine derivatives **(88)** from the catalyst-free ultrasound-activated reaction between differently substituted primary amines **(89)**, carbon disulfide **(90)**, and the dialkyl acetylene carboxylates **(91)** (Scheme 21) [64].



Scheme 21 Catalyst-free synthesis of the biologically active rhodanine.

4.1.7 Synthesis of 4H-3,1-benzoxazin-4-ones

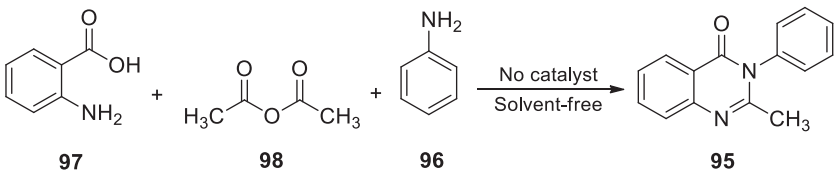
Among all the different classes of bioactive heterocyclic compounds, the class containing derivatives of 4*H*-3,1-benzoxazin-4-one has significant importance because of the wide-ranging applications it exhibits [65]. Even though this class has a broad range of applicabilities, yet there are very few methods available for its synthesis. In 2012, Azarifar and Sheikh introduced a facile one-pot ultrasonicated synthesis (Scheme 22) [66] to afford 2,2′-(1,4-Phenylene)bis[1acetyl-1,2-dihydro-4*H*-3,1-benzoxazin-4-one] **(92)** via condensation reaction between 2-aminobenzoic acid **(93)** and benzene-1,4-dicarboxaldehyde **(94)** in the presence of an excess of Ac_2O.



Scheme 22 Synthesis of derivatives of 2,2′-(1,4-Phenylene)*bis*[1acetyl-1,2-dihydro-4*H*-3,1-benzoxazin-4-one].

4.1.8 Synthesis of quinazolines-based heterocycles

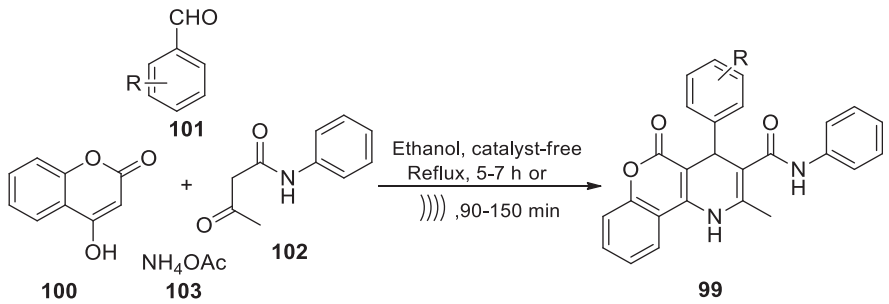
Recently, Purkhosrow and coworkers in 2019 have reported this efficient ultrasonicated synthesis of the novel family of quinazoline **(95)**. In contrast to the conventional methods, this approach afforded the resulting product in excellent yields. In this approach, primary amines **(96)**, anthranilic acid **(97),** and acetic anhydride **(98)** underwent sonication producing the required compounds (Scheme 23) [67]. Importantly, the synthesized molecules were found to exhibit the vaso-relaxant bioactivity.



Scheme 23 One-pot, catalyst-free synthesis of new derivatives of quinazoline.

4.1.9 Synthesis of pyrido[2,3-c] coumarins

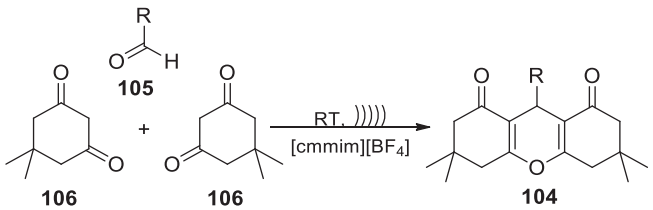
An easy, efficient, multicomponent environment-benign, catalyst-free strategy for the production of a novel family of pyrido[2,3-*c*] coumarin **(99)** was reported by Chidurala and his colleagues in 2015. In this one-pot multicomponent approach, 4-hydroxy-2*H*-chromen-2-one **(100)**, benzaldehyde **(101)**, acetoacetanilide **(102)**, and ammonium acetate **(103)** were condensed together in ethanol as a solvent in the presence of ultrasonic irradiation (Scheme 24) [68].



Scheme 24 Ultrasonically irradiated catalyst-free synthesis of pyrido[2,3-*c*] coumarins.

4.1.10 Synthesis of octahydroxanthenes

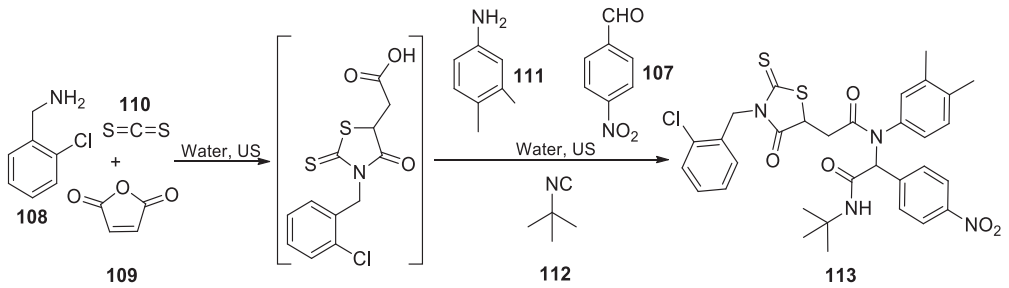
Xanthene and its derivatives are known for their presence in many naturally occurring bioactive compounds and possess the large number of pharmacological activities such as antimalarial [69], antiviral [70], anti-inflammatory [71], and anti-plasmodial [72] activities. Therefore, many synthetic protocols have been reported from time to time in order to generate these biologically significant heterocyclic compounds. Dadhania and coworkers reported the green synthesis of 1,8-dioxo-octahydroxanthene **(104)** via condensation of differently substituted aldehydes **(105)**, dimedone **(106)** in 1-carboxymethyl-3-methylimidazolium tetrafluoroborate at room temperature without any catalyst (Scheme 25) [73].



Scheme 25 Sonochemical catalyst-free protocol synthesizing 1,8-dioxo-octahydroxanthenes.

4.1.11 Synthesis of pseudopeptides containing rhodanine

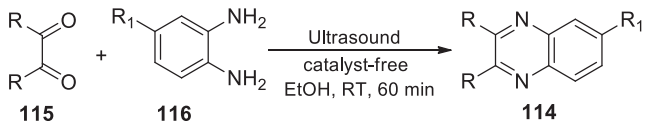
Starting from the easily available starting materials, Shaabani and Hooshmand in 2017 reported a well-planned, environment-benign synthetic pathway for the synthesis of pseudopeptides incorporating rhodanine by using tandem Michael-Ugi reactions in sequential order (Scheme 26) [74]. In this synthetic route, aromatic aldehyde **(107)**, primary amines **(108)**, maleic anhydride **(109)**/itaconic anhydride, carbon disulfide **(110)**, substituted anilines **(111)**, and isocyanides **(112)** were treated under sonochemical conditions for 90–120 min under catalyst-free conditions to afford the requisite organic compounds **(113)**.



Scheme 26 Synthesis of pseudopeptides incorporating rhodanine using sonication.

4.1.12 Synthesis of derivatives of quinoxaline

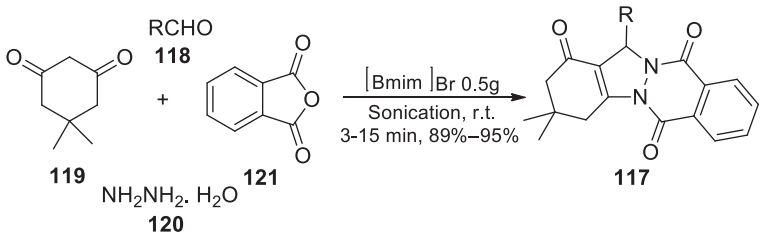
Quinoxaline belongs to one of the pharmaceutically active families of the heterocyclic compounds [75] and hence many synthetic methodologies are available in the literature. These procedures involves the use of $CuSO_4.5H_2O$ [76], ceric ammonium nitrate [77], $POCl_3$ [78], MnO_2 [79], etc. as catalysts. However, in a view to develop safe synthetic methodologies, Guo et al. reported the ultrasonically promoted, green, facile, efficient, and catalyst-free synthesis of quinoxaline **(114)** by the reaction of aliphatic 1,2-diketones **(115)** and 1,2-diamines **(116)** at room temperature in ethanol as solvent (Scheme 27) [80].



Scheme 27 Sonochemically irradiated catalyst-free protocol for the synthesis of quinoxalines.

4.1.13 Synthesis of 2H-indazolo[2,1-b]phthalazine-triones

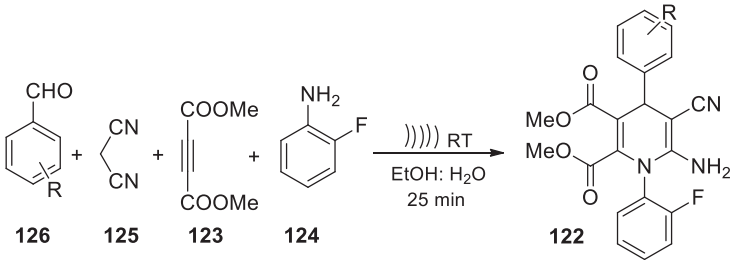
Shekouhy et al. demonstrated the catalyst-free synthesis of a biologically significant family of 2*H*-indazolo[2,1-*b*]phthalazine-triones **(117)** via sonication. In this ultrasound-assisted one-pot multicomponent method, different derivatives of aldehyde **(118)**, dimedone **(119)**, hydrazine hydroxide **(120)**, and phthalic anhydride **(121)** are reacted in the presence of [Bmim]Br at room temperature in a neutral medium to afford the desired product (Scheme 28) [81].



Scheme 28 Synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones in ionic liquid without any catalyst.

4.1.14 Synthesis of 1-(2-fluorophenyl)-1,4-dihydropyridines

A straightforward, eco-friendly, one-pot four-component methodology synthesizing a functionalized series of 1-(2-fluorophenyl)-1,4-dihydropyridines **(122)** was developed by Shabalala and his coworkers (Scheme 29) [82]. This multicomponent approach involves the condensation of dimethylacetylenedicarboxylate **(123)**, 2-fluoroaniline **(124)**, malononitrile **(125),** and various substituted aldehydes **(126)**.

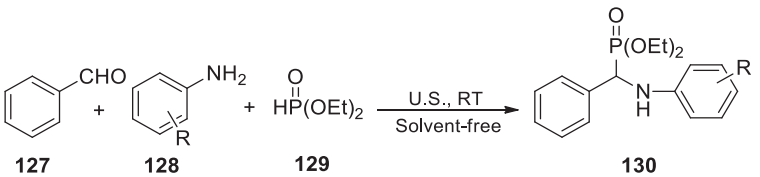


Scheme 29 Catalyst-free sonochemical synthesis of 1-(2-fluorophenyl)-1,4-dihydropyridines.

4.2 Applications of ultrasound in catalyst-free synthesis of molecules other than heterocycles

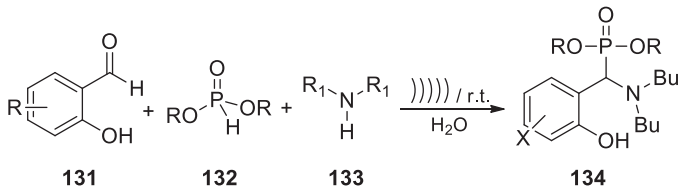
4.2.1 Synthesis of α-amino phosphonates

Among the various classes of the organic compounds, α-amino phosphonates have captivated the remarkable attention of the researchers due to their wide spectrum of bioactivities [83]. The synthesis of this class is generally supported by the addition of the catalysts. Xia et al. introduced a one-pot three-component catalyst-free protocol in which the ultrasonic irradiation of the different aldehydes **(127)**, suitably substituted amines **(128)**, and diethyl phosphate **(129)** afforded the synthesis of α-amino phosphonates **(130)** at room temperature in better yields (Scheme 30) [84].



Scheme 30 Simple and efficient synthesis of the α-amino phosphonates through sonication.

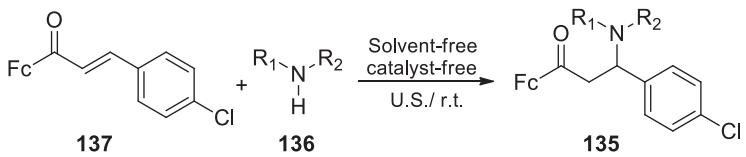
Owing to the diverse range of the biological activities exhibited by tertiary α-amino phosphonates [85, 86], the area involving the synthesis of these compounds has significant importance. In a recent report, Kalla along with his coworkers employed ultrasonication for its generation via improved Kabachnik-Fields reaction (Scheme 31) [87]. In this modified version of Kabachnik-Fields reaction, suitably substituted salicylaldehyde **(131)**, di or tri-alkyl phosphites **(132)**, and di-*n*-butylamine **(133)** were reacted and resulted into the synthesis in good to excellent yields **(134)**.



Scheme 31 Ultrasonically activated catalyst-free synthesis of tertiary α-amino phosphonates.

4.2.2 Synthesis of ferrocenyl containing carbonyl compounds

Yang et al. explored a novel catalyst-free and solvent-free protocol (Scheme 32) [88] generating diversely substituted 1-Ferrocenyl-3-amino carbonyl compounds **(135)** via aza-Michael interaction of aliphatic amines **(136)** with the unsaturated *α,β*-carbonyl compounds **(137)** at room temperature.



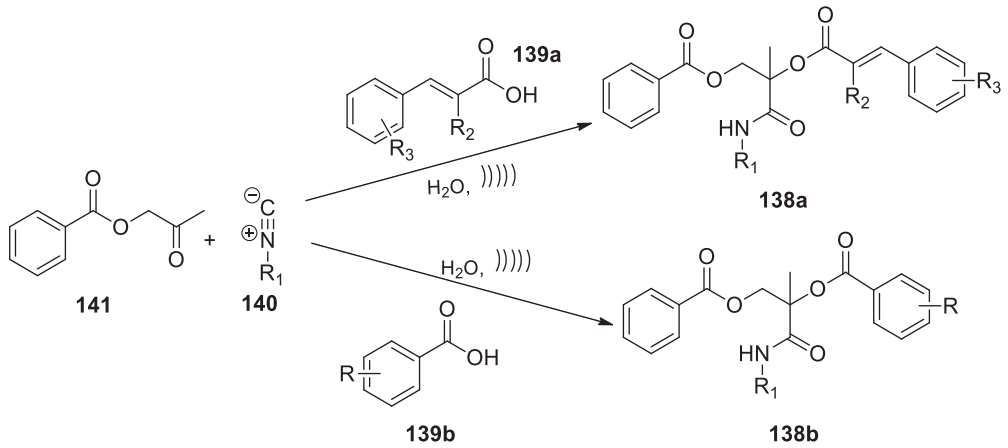
Scheme 32 Catalyst-free Synthesis of 1-Ferrocenyl-3-amino carbonyl compounds via ultrasonication.

4.2.3 Synthesis of propanamides

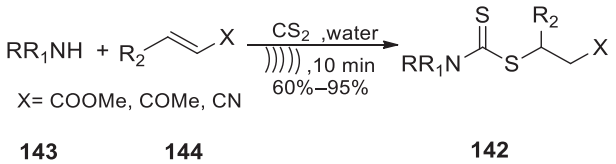
Ramazani et al. demonstrated an atom-efficient, facile, highly selective, catalyst-free multicomponent approach constructing the propanamide derivatives **(138a, 138b)** in excellent yields from the easily accessible starting materials (Scheme 33) [89]. In this protocol, a mixture of suitably substituted carboxylic acid **(139a,139b)**, isocyanide **(140)**, and the 2-oxopropyl benzoate **(141)** are condensed together sonochemically in water resulting into desired reaction results.

4.2.4 Synthesis of dithiocarbamates

A rapid, convenient, one-pot, multicomponent approach for the synthesis of dithiocarbamates **(142)** and its derivatives was reported by Azizi and his coworkers (Scheme 34) [90]. This multicomponent approach involved the treatment of carbon disulfide with the primary and secondary amines **(143)** along with unsaturated carbonyl compounds **(144)** or alkyl halides **(144)** in water.



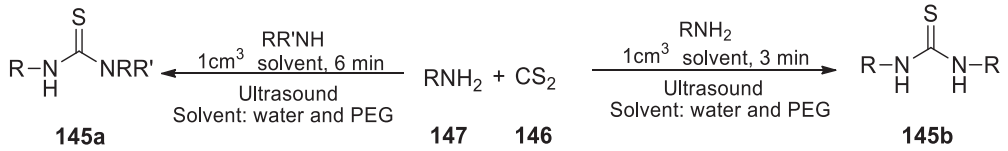
Scheme 33 Synthesis of propanamide derivatives with high substitution in water as solvent.



Scheme 34 Ultrasound-assisted synthesis of dithiocarbamates.

4.2.5 Synthesis of thiourea

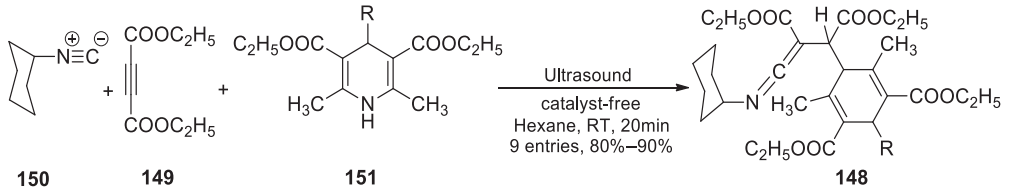
Thiourea and their derivatives form a biologically significant class of heterocyclic compounds [91–93] and thus have attracted the attention of chemists to devise various protocols for its synthesis. Traditionally, the synthesis of derivatives of thiourea **(145a, 145b)** involved the usage of toxic reagents and substrates but being a biologically active molecule, an eco-friendly protocol was required for its synthesis. As a result of the sustained efforts, Azizi et al. successfully reported the methodology involving ultrasonic-promoted condensation of carbon disulfide **(146)** with aliphatic primary amines **(147)** in water and PEG (green solvents) (Scheme 35) [94].



Scheme 35 Ultrasonically-assisted synthesis of thiourea derivatives.

4.2.6 Synthesis of ketene imines

Ketene imines act as the reactive intermediates in the synthesis of the nitrogen-containing heterocycles [95] and can undergo reactions with electrophiles, nucleophiles, and free radicals. Therefore, many synthetic strategies are available for the generation of these intermediates. Recently, Emtiazi and his coworkers introduced a one-pot, ultrasonic protocol for the synthesis of ketene imines **(148)** via condensation of diethyl acetylenedicarboxylate **(149)**, cyclohexyl isocyanide **(150)**, and 1,4-dihydropyridines **(151)** yielding the ketene imines in excellent yields (Scheme 36) [96].



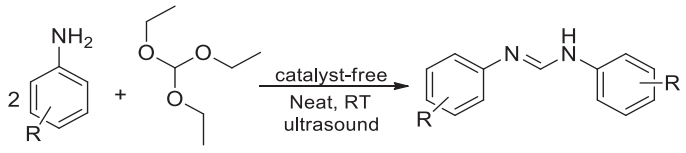
150 149 151 148

Scheme 36 One-pot sonochemical synthesis of ketene imines.

4.2.7 Synthesis of series of formamidines

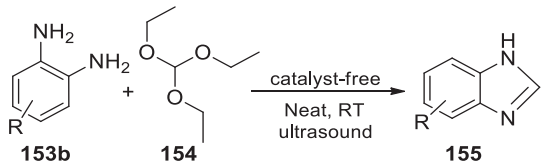
The organic compounds exhibiting formamidine has captivated the remarkable attention of the medicinal chemists and researchers owing to their versatile applicabilities, e.g., serve as the linking unit in polymer synthesis [97], bleaching agents for papers [98], and starting material for various chemical transformations [99]. In addition to this, they also have significant applications in the cryoscopic determination of molecular weights in benzene [100] and in solid-phase synthesis [101]. Unfortunately, the majority of the synthetic methods available involve harsh reaction conditions, toxic and protic solvents, and monotonous work-up procedures.

In 2013, Dar and his coworkers reported an ultrasound-promoted solvent-free and catalyst-free approach synthesizing the desired moiety **(152)** with the differently substituted aryl amines **(153a,153b)** and triethyl orthoformate **(154)** (Scheme 37) [102]. This methodology was further extended for the synthesis of the benzimidazoles **(155)** (Scheme 38) [102].



153a 154 152

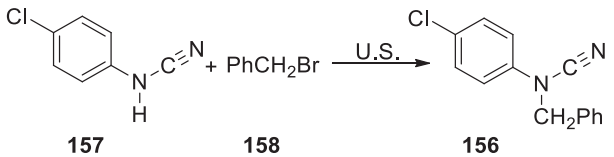
Scheme 37 Solvent-free and catalyst-free synthesis of diaryl-substituted formamidines via sonication.



Scheme 38 Synthesis of family of benzimidazole using sonication.

4.2.8 *Synthesis of* N-*benzyl*-N-*(4-chlorophenyl)cyanamide*

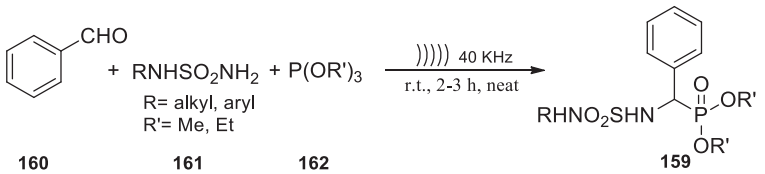
In organic synthesis, cyanamides and their derivatives constitute a significant class of organic molecules. They act as the building block for therapeutically important nitrogen-containing heterocycles [103, 104]. In addition to this, the organic compounds incorporating cyanamides show a wide spectrum of biological activities like herbicidal [105], anticancer [106], and antiviral [107] activities. Therefore, many synthetic methodologies have been reported for this class making use of hazardous reagents and solvents, and drastic reaction conditions. To overcome these problems, Nasrollahzadeh in 2019 made use of the ultrasonic irradiation for the synthesis of *N*-benzyl-*N*-(4-chlorophenyl)cyanamide **(156)** (Scheme 39) [108]. In this protocol, arylcyanamides **(157)** undergo *N*-benzylation via reaction with benzyl bromide **(158)** in C_2H_5OH at room temperature without any added catalyst.



Scheme 39 Ultrasonic catalyst-free synthesis of *N*-benzyl-*N*-(4-chlorophenyl)cyanamide.

4.2.9 *Synthesis of α-sulfamidophosphonate*

Belhani and his group in 2015 demonstrated the ultrasonically irradiated catalyst-free and solvent-free protocol synthesizing the biologically significant novel series of *α*-sulfamidophosphonate **(159)**. This one-pot multicomponent methodology resulted successfully in the synthesis of the desired compounds with excellent yields through the condensation of aromatic aldehydes **(160)** with the sulfonamide **(161)** and suitable triethylphosphite **(162)** at room temperature (Scheme 40) [109].



Scheme 40 Sonochemical synthesis of α-sulfamidophosphonate.

5. Conclusion

In the present era, catalyst-free reactions have gained significant attention among researches especially working in the field of green chemistry. This is mainly due to the fact that chemists are continually striving to modify the traditional synthetic strategies to make organic synthesis more environment benign by avoiding the use of toxic and hazardous catalysts and/or reagents. Ultrasound-assisted catalyst-free protocols have also emerged as alternative nonconventional techniques to augment the traditional methods in organic synthesis. In this chapter, we have encapsulated the latest development in the field of sonochemical catalyst-free organic synthesis and also tried to highlight the advancement of these nonconventional techniques for the synthesis of biologically relevant molecules.

Acknowledgment

R. Sharma thanks SMVD University for fellowship.

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CHAPTER 3

Sonochemical protocol for stereoselective organic synthesis

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1. Introduction

Energy plays a vital role in all chemical reactions. Every chemical reaction is associated with several energy changes occurring due to the cleavage of old bonds and the formation of new bonds. Energy can either be released or absorbed during a reaction. The energy required for the successful completion of any reaction can be provided from various sources. One such highly efficient source is ultrasound waves which are sound waves having a frequency >20 kHz and wavelength between 7.0 and 0.015 cm. Spectacular accelerations have been produced in many reactions as a consequence of heating through ultrasound waves [1–4]. The first technical application of these waves date back to 1917 where they were first employed by Paul Langevin for the detection of submarines which later led to the development of SONAR (sound navigation and ranging) technique. Various other applications of ultrasound include welding, cutting, drilling of hard materials, cell disruption, cleaning and drilling of teeth, dispersion of solids in inks, paints, and resins, ultrasound imaging of fetus and healing of muscle strains, welding of thermoplastics, degradation of polymers, etc. [5–11].

Sonochemistry is the branch of chemistry, which deals with the study of the effect of ultrasounds on chemical reactions. Off late, a diverse range of chemical reactions especially stereoselective organic syntheses have been carried out using these waves. Usage of these waves have several advantages over the conventional methods such as less time consuming, eco-friendly, requires less temperature and pressure due to which they have created a niche in green chemistry [12, 13].

The process responsible for the enhancement of chemical reactions in the presence of ultrasounds is known as cavitation during which gaseous cavities or bubbles are created, enlarged, and exploded. Heightened local temperatures and pressures are induced inside the cavities creating localized hot spots in which the mechanical energy of sound is transformed into a useful chemical form [14, 15]. Sonochemical reactions can be classified into three types [16, 17]

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(1) Homogeneous reactions: Radical or radical-ion intermediates are formed during these reactions.
(2) Heterogeneous reactions (liquid-liquid or solid-liquid system): Ionic intermediates are formed during these reactions.
(3) Sonocatalysis: These include both a radical and ionic mechanism.

In this chapter, we shall focus on the effect of ultrasounds on stereoselective reactions. Firstly, we must understand the different modes of selectivity namely, chemoselectivity, regioselectivity, and stereoselectivity. Chemoselectivity is the property of a reagent or an intermediate to react preferentially with one group or atom out of the different groups or atoms present in the same molecule. Regioselectivity is the ability of a reaction to form or break bonds in one direction in preference to all other possible directions.

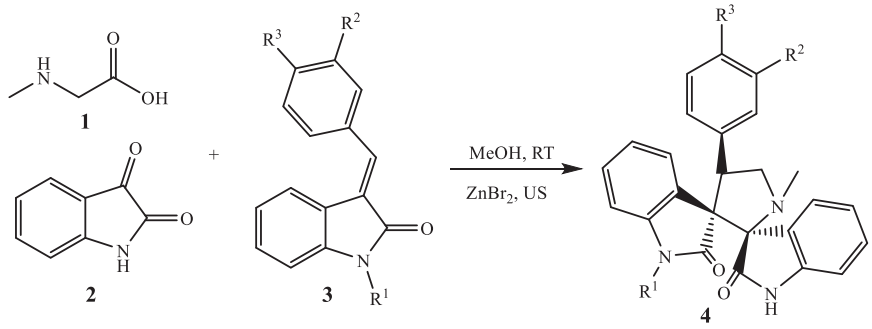
During stereoselectivity one or more new elements of chirality are created in a substrate which leads to the production of an unequal mixture of stereoisomers. According to Rauws [18] "Stereoselectivity is the extent to which an enzyme or other macromolecule, or macromolecular structure (antibody or receptor) exhibits affinity towards one molecule of a pair of isomers in comparison with and in contrast to the other isomer."

A stereoselective reaction can be either enantioselective (one enantiomer is formed in preference to the other) or diastereoselective (one diastereomer is formed in preference to another). Enantiomers have opposite configuration at chiral centers, i.e., *R*-configuration or *S*-configuration while in diastereomer differ from one or more chiral centers. Enantioselective or diastereoselective is very important in the medical industry as both isomers have different biological activity [19–21].

Therefore, the development of stereoselective synthesis with ultrasonic irradiation toward greener approach developed recently and in the past are included in this chapter. This chapter highlights activity using ultrasound-assisted stereoselective synthesis and discusses their advantages, limitations, and plausible mechanisms. This chapter also describes the approaches which can be implemented to improve selectivity, i.e., enantioselectivity and diastereoselective. The importance of ultrasonic irradiation in stereoselective synthesis is shown by selected examples.

2. Stereoselective organic synthesis under ultrasonication

A methodology for the stereoselective synthesis of dispiropyrrolidine bisoxindole derivatives **4** via cycloaddition reaction of azomethine ylide (formed by the reaction of sarcosine **1** and isatine **2**) with (*E*)-3-benzylideneindolin-2-ones **3** has been developed by Kiamehr and coworkers [22] under sonication using $ZnBr_2$ as catalyst (Scheme 1). To check the effect of ultrasound, they also performed this reaction under reflux condition but reaction took longer reaction time to completion with lesser yield.

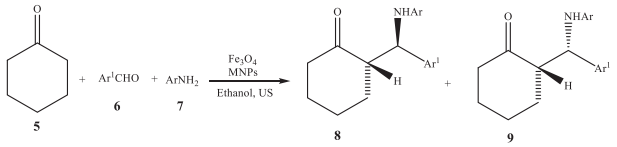


Scheme 1 Synthesis of dispiropyrrolidinebisoxindole derivatives.

Mechanistically, reaction completed through oxazolidinone intermediate which undergoes 1,3-dipolar cycloaddition to afford final product.

Shariati and coworkers [23] have developed an ultrasound-assisted methodology for the stereoselective synthesis of β-amino carbonyl **8,9** using Mannich reaction using iron oxide magnetite nanoparticles (Scheme 2). The synthesis of β-amino carbonyls **8,9** was achieved by multicomponent reaction of cyclohexanone **5** with different aldehydes **6** and amines **7** in ethanol.

The coupling constant of the vicinal protons adjacent to C=O and NH in proton NMR revealed that the stereochemistry of the Mannich product was *syn* and *anti* and the value of coupling constant for *anti*-isomers was bigger than *syn*-isomers.



Scheme 2 Synthesis of β-amino carbonyl derivatives.

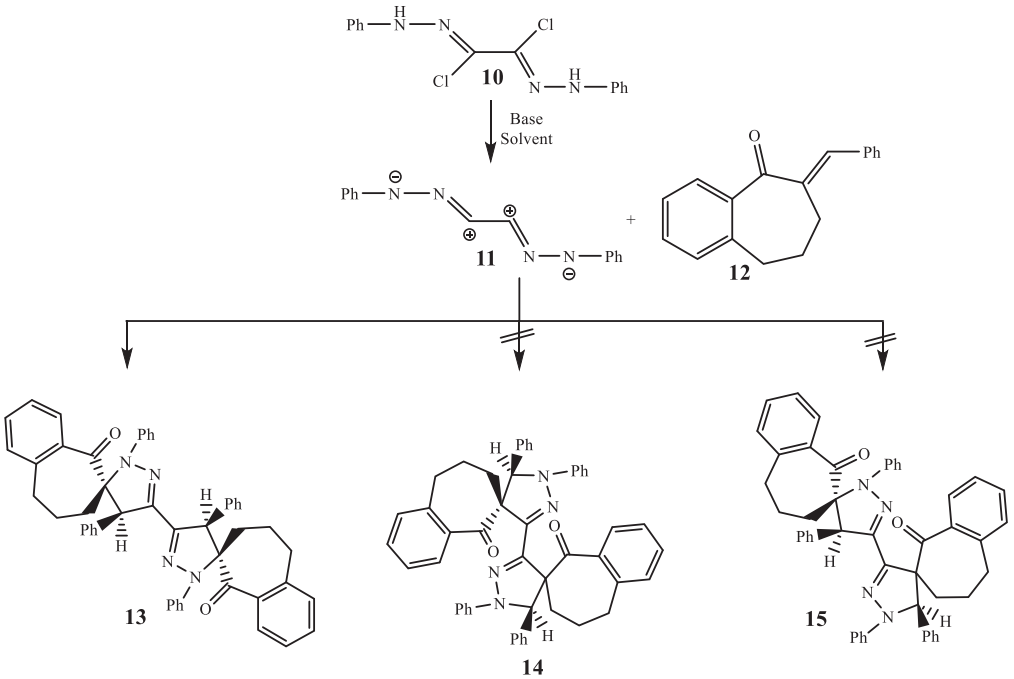
Further, the same reaction also reported by Hashemi and coworkers [24] using zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) as a catalyst with 100% anti selectivity under solvent-free conditions using sonication as an energy source. While the reaction in aqueous and other solvent showed less stereoselectivity. Further, Ozturkcan and coworkers [25] also reported the same Mannich reaction using bismuth(III) triflate as a catalyst in water under ultrasound irradiation with excellent antiselectivity. Low selectivity was found with the heteroaromatic aldehydes or amines.

Same Mannich reaction also reported by Ghomi and coworkers [26] using Fe_3O_4 nanoparticles supported ionic liquid under ultrasonication. Mechanistically, Mannich products formed via *si*-face of imine attack on re-face of cyclohexanone because the other

face, i.e., *re*-face of imine could not attack *si*-face of cyclohexanone due to steric interactions between the aromatic ring and ionic liquid moiety.

Behbehani and coworkers [27] have synthesized bis spiro-benzosuberane pyrazoline derivatives **13** by the reaction of bis-hydrazonoyl chlorides **10** with 2-arylidene suberones **12** under sonication in ethanol and triethylamine as the base (Scheme 3). This stereoselective synthesis was achieved *via* a 1,3-dipolar cycloaddition reaction between bis-nitrilimine and 2-arylidene suberones.

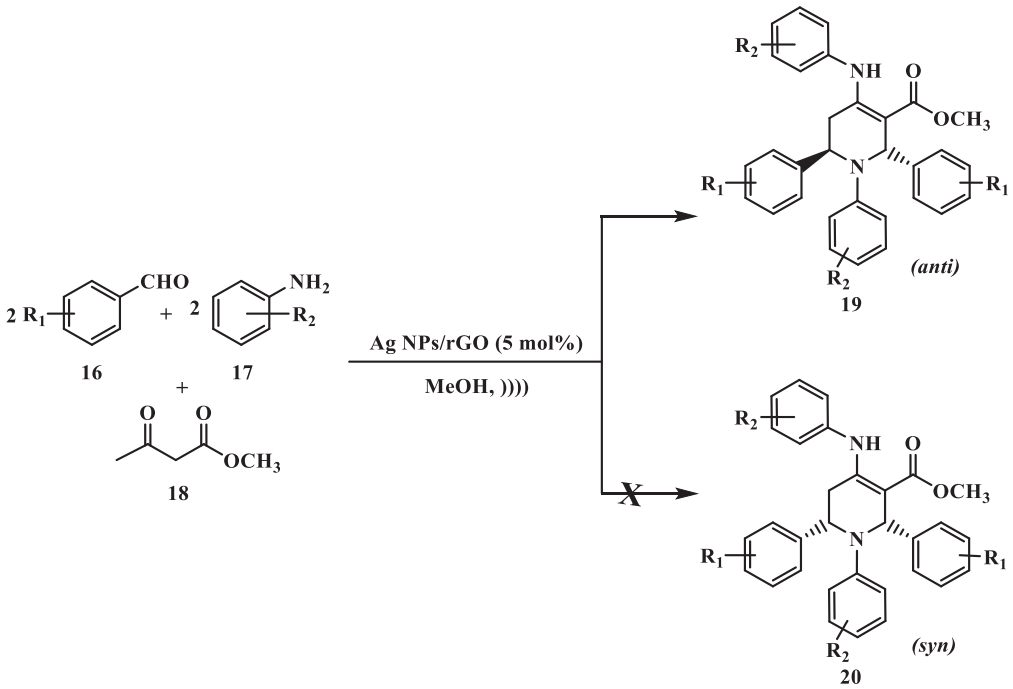
Mechanistically, bis-nitrilimine **11** have two attacking sites where 2-arylidene suberones **12** attacks to form the desired product. There is the chance of the formation of three cycloadducts but according to proton NMR data, product **13** formed as sole product. Further, they also performed this reaction under reflux condition, took 36 h to completion with a lower yield.



Scheme 3 Synthesis bis spiro-benzosuberane pyrazoline derivatives.

Dandia and coworkers [28] have synthesized Ag NPs decorated reduced graphene oxide (Ag NPs/rGO) and used into the diastereoselective synthesis of tetrahydropyridines **19** by the reaction of substituted aldehydes **16**, anilines **17,** and methyl acetoacetate **18** under ultrasonication using methanol as solvent (Scheme 4). Many catalysts

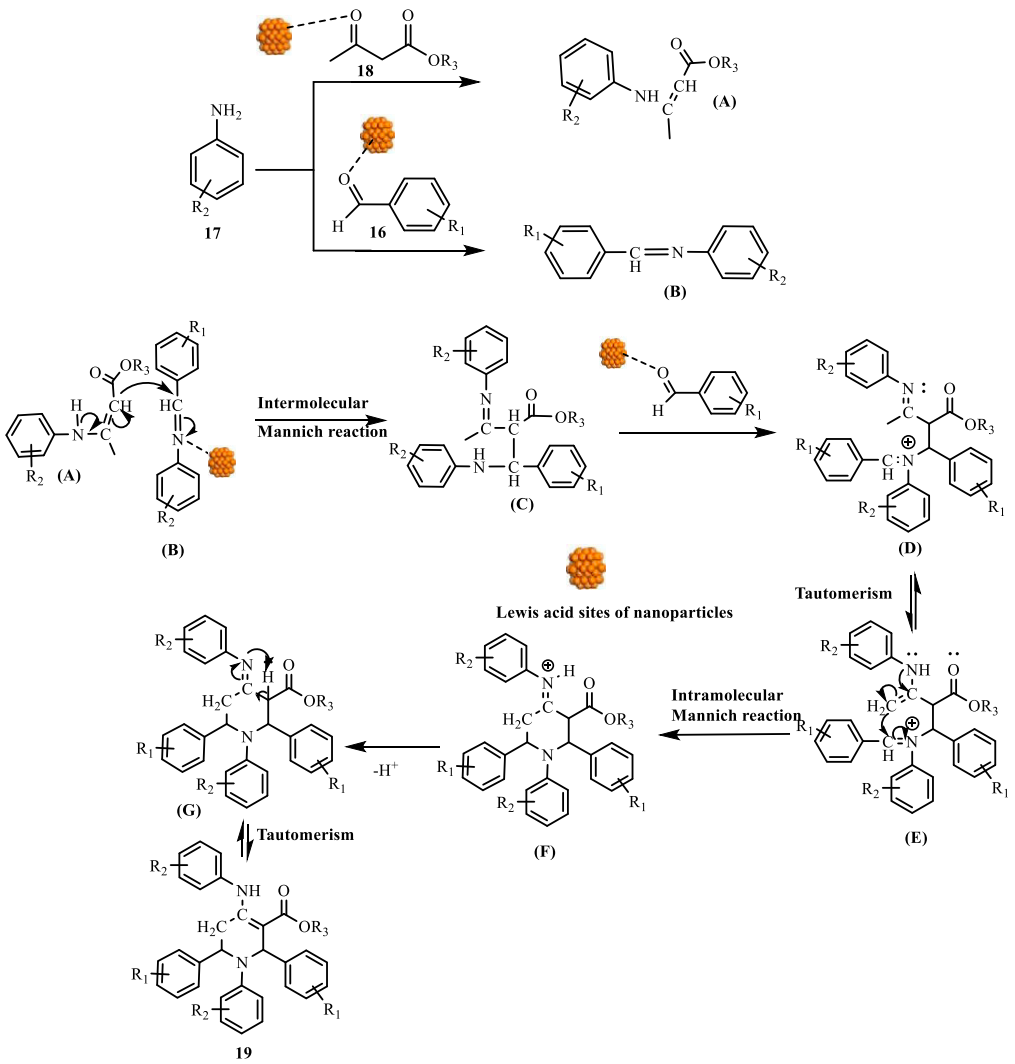
tried for this multicomponent reaction under conventional and ultrasonic irradiation but conventional catalysts could mainly afford the target compound **19** in low yields. In total 5 wt% of Ag NPs/rGO produced product in excellent yield within shorter reaction time.



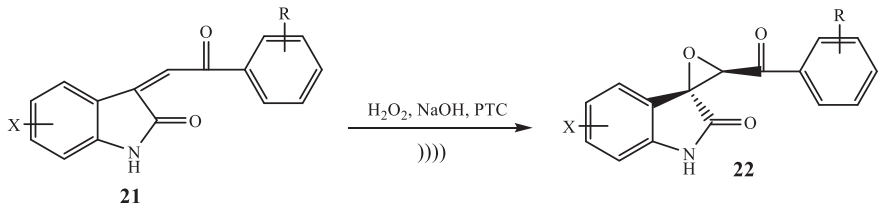
Scheme 4 Diastereoselective synthesis of tetrahydropyridine derivatives.

Mechanistically, nanoparticles behave as Lewis acid catalysts to activate ketoester **18** and aldehydes **16** by binding with the oxygen of carbonyl groups and form enamine (**A**) and imine (**B**). Mannich reaction between **A** and **B** to afford **C** which reacts with activated aldehyde to afford **D** by the elimination of H_2O. Intermediate **D** tautomerized to provide **E** which gave intramolecular Mannich addition to afford final tetrahydropyridine product **19** (Scheme 5) and according to proton NMR spectra, the stereochemistry of product is *anti*-diastereoselective.

Dandia and coworkers [29] have established a pathway for the diastereoselective preparation of spiro oxirane derivatives **22** by the epoxidation reaction of 3-aroylmethylene indole-2-ones **21** using hydrogen peroxide as epoxidation reagent (Scheme 6). Initially, the epoxidation reaction of 3-aroylmethylene indole-2-ones was done using 30% H_2O_2 and sodium hydroxide under sonication but the yield was very low. Further, they used



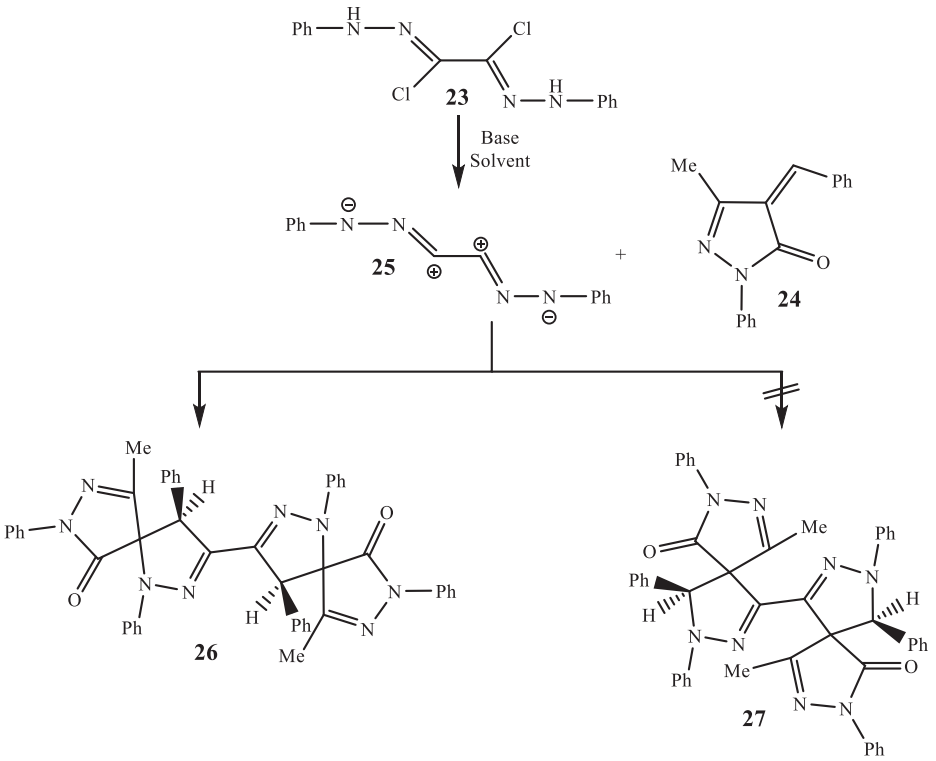
Scheme 5 Plausible mechanism for the synthesis of tetrahydropyridine derivatives.



Scheme 6 Diastereoselective synthesis of spiro-oxirane derivatives.

phase transfer catalyst cetyltrimethylammonium bromide in 0.05 mmol and surprisingly, an excellent yield of oxirane obtained. Dandia and coworkers observed that this methodology showed high diastereoselective and the trans stereochemistry of the product.

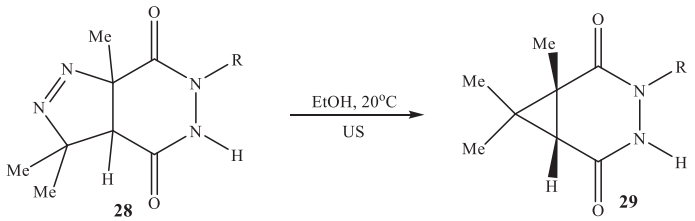
Behbehani and coworkers [30] have synthesized bis spiro-pyrazoline derivatives **26** by the reaction of bis-hydrazonoyl chlorides **23** with 4-arylidenepyrazol-5-one derivatives **24** under sonication using ethanol as reaction medium and triethylamine as the base (Scheme 7). This stereoselective synthesis was achieved *via* 1,3-dipolar cycloaddition reaction between bis-nitrilimine **25** which generated in situ from bis-hydrazonoyl chlorides **23** and 4-arylidenepyrazol-5-one derivatives **24**. There is the chance of the formation of two cycloadducts but according to proton NMR data, product **26** formed as sole product.



Scheme 7 Synthesis of bis spiro-pyrazoline derivatives.

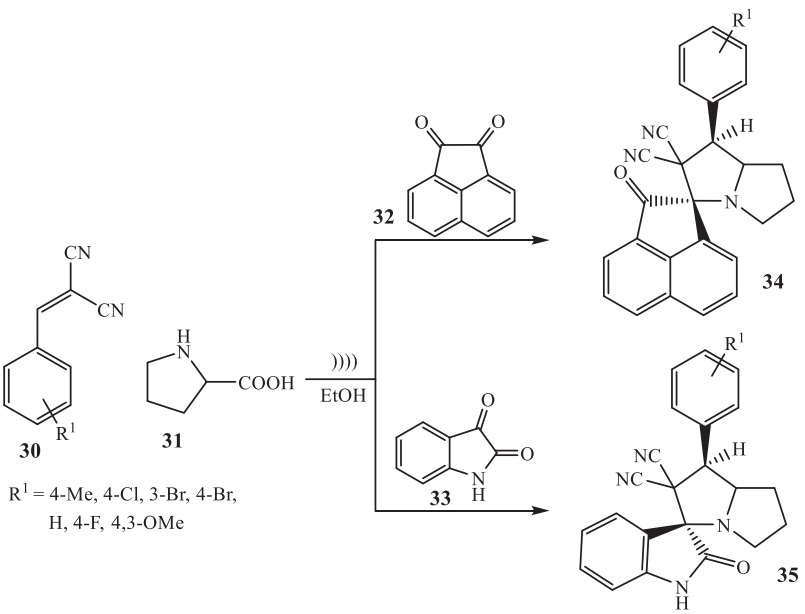
Stereoselective methodology for the synthesis of bicyclo-cyclopropanes **29** was developed by Hamadi and coworkers [31] from pyrazolines **28** under ultrasound irradiation using ethanol as solvent at 200 W power and 30 kHz frequency (Scheme 8). The cis

relationship between the proton H-6 and the Me groups was confirmed by NOESY spectrum as observed NOE effect between Me groups and the proton H-6.



Scheme 8 Stereoselective synthesis of bicyclo-cyclopropane derivatives.

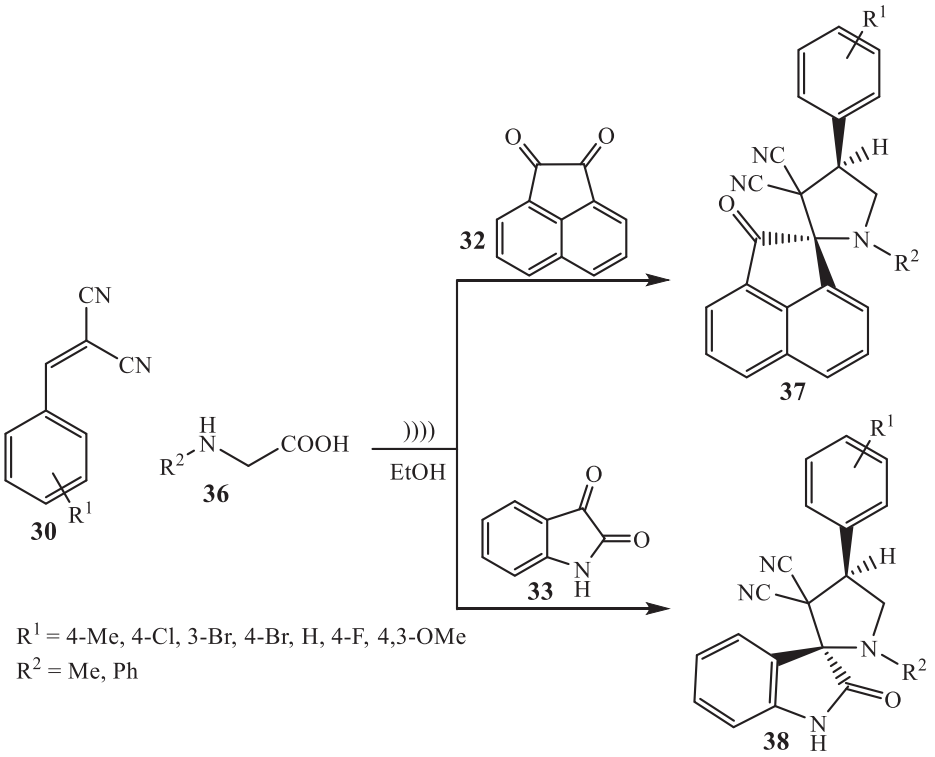
Nabid and coworkers [32] have synthesized highly diastereoselective and regioselective spiropyrrolidine **34** and spiropyrrolizidine derivatives **35** by the reaction of arylidene malononitrile **30** with azomethine ylides under ultrasonic irradiation *via* 1,3-dipolar cycloaddition reaction (Scheme 9). Initially, the reaction of aldehydes with malononitrile to generate arylidene malononitrile (dipolarophiles) **30** and azomethine ylides which prepared by the reaction of proline **31** with acenaphthoquinone **32** or isatin **33**. 1,3-dipolar cycloaddition reaction between dipolarophiles and azomethine ylides tried under conventional heating using methanol as a solvent but took a longer time. Further, they tried this reaction under ultrasonication using ethanol and product obtained in good yield



Scheme 9 Diastereoselective and regioselective synthesis of spiropyrrolidines and spiropyrrolizidines.

within a shorter reaction time. Furthermore, to check the effect of ultrasound frequency, firstly performed reaction at 25 kHz, the reaction gave the product in good yield. Increasing the frequency up to 45 kHz did not change the product yield.

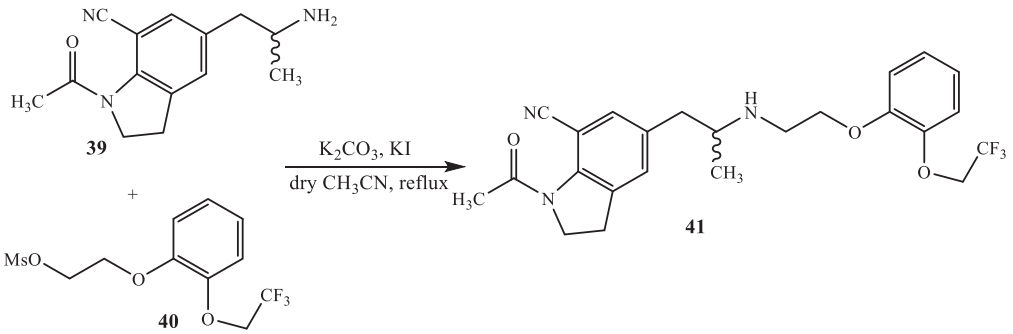
Further, they used sarcosine or N-phenylglycine **36** in place of proline **31** for the synthesis of spiropyrrolidine **37** and spiropyrrolizidine derivatives **38** under ultrasonication using ethanol as solvent (Scheme 10). Mechanistically, reaction completed by two mechanisms, concerted or diradical. Concerted pathways followed under the conventional condition and diradical pathways followed under ultrasonic conditions were confirmed by using *p*-benzoquinone as a radical scavenger. Finally, spectroscopic data showed that the oxindole moiety is planar and perpendicular to the pyrrolidine ring.



Scheme 10 Synthesis of spiropyrrolidines and spiropyrrolizidines.

Sun and coworkers [33] have developed an approach for the enantioselective synthesis of (−)-(*R*) silodosin and this is done by diastereomeric crystallization using (*S*)-(+)-mandelic acid under ultrasonic irradiation (Scheme 11). Initially, silodosin as racemic mixture **41** was obtained by the condensation of aminopropyl indoline carbonitrile **39**

substituted by acetyl group at nitrogen with trifluoroethoxy phenoxy ethyl methanesulfonate **40** using dry acetonitrile as the solvent, K_2CO_3 as base, and KI as an additive (**Scheme 8**).

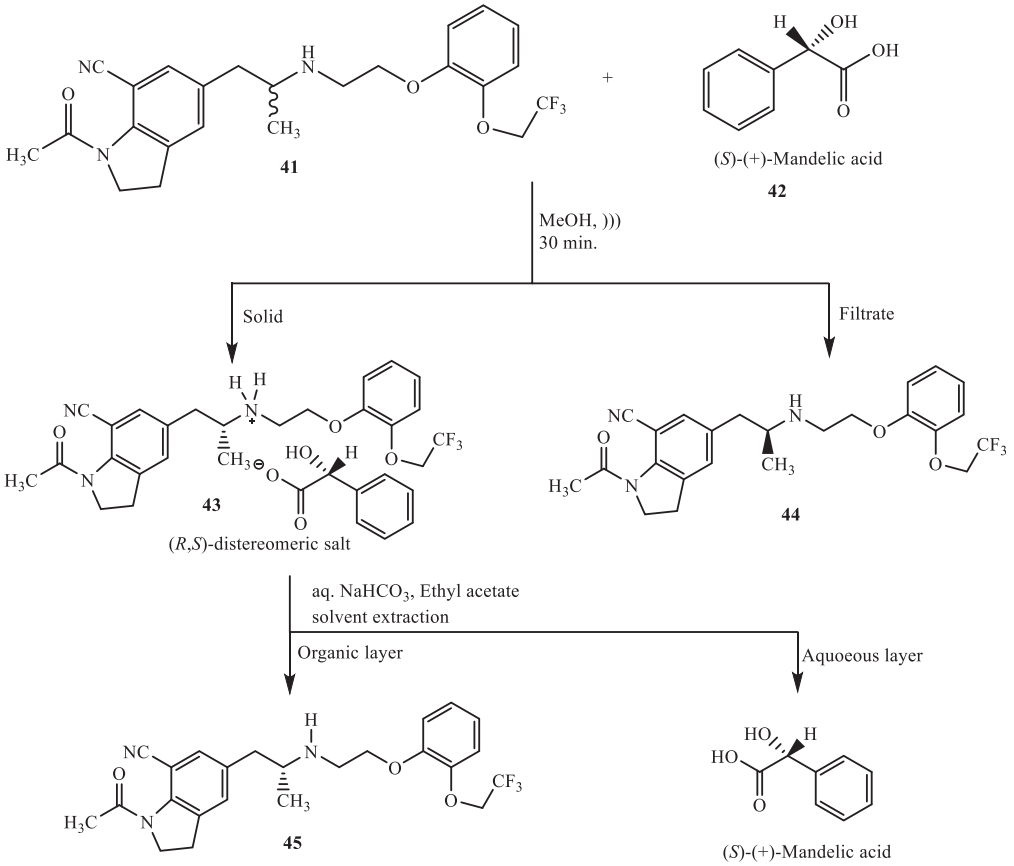


Scheme 11 Enantioselective synthesis of (–)-(*R*) silodosin.

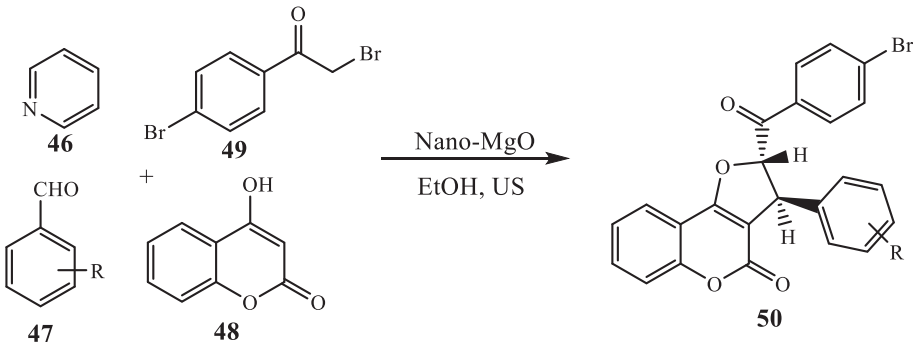
After synthesis of silodosin, the racemic mixture was separated by diastereomeric crystallization using (*S*)-(+) mandelic acid **42**. Initially, this separation tried conventionally in methanol but this method has some disadvantages such as diastereomeric salt **43** was obtained as a gummy solid and most of the salt remains in methanol. Further, they introduced ultrasound for the diastereomeric crystallization using methanol as solvent, (*R,S*)-diastereomeric salt **43** was separated as solid and (*S*)-silodosin **44** was found in filtrate. Further, (*R*)-silodosin **45** was obtained by solvent extraction using aqueous $NaHCO_3$ and ethyl lactate (Scheme 12).

Safaei-Ghomi and coworkers [34] have developed MgO nanoparticles catalyzed diastereoselective synthesis of *trans* furocoumarins **50** under sonication by the one-pot reaction of pyridine **46**, benzaldehydes **47**, 4-hydroxycoumarin **48**, and 2,4-dibromoacetophenone **49** (Scheme 13). Initially, reactions carried out in diverse solvents such as ethanol, acetonitrile, dimethylformamide, and water in the presence of different catalysts but the best result was found in ethanol using MgO nanoparticles as a catalyst. Stereochemistry of furocoumarins **50** was confirmed by calculating the lower heat of the formation of trans-isomer using PM3 calculations [35]. Mechanistically, the formation of trans products involved a S_N2 mechanism.

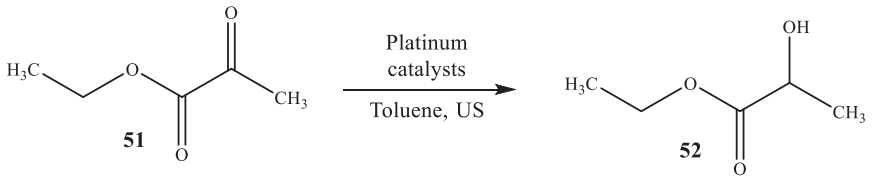
Bartok and coworkers [36] reported enantioselective hydrogenation of an aliphatic α-ketoester **51** to ethyl lactate **52** under sonication using platinum catalysts (Scheme 14). They used different platinum catalysts such as Pt/C, Pt/SiO_2, and Pt/K-10 but reaction proceeded faster with Pt/SiO_2 and Pt/K-10 catalyst underneath pre-sonicated condition. They also used these catalysts under conventional heating but it took longer reaction time to completion. Further, they tried different solvents but higher ee (enantiomeric excess) values obtained in toluene and the enantioselectivity increased in Pt/SiO_2 and Pt/K-10 catalyst, respectively, as compared to Pt/C catalyst.



Scheme 12 Separation of (*R*)-silodosin using (*S*)-(+) mandelic acid.

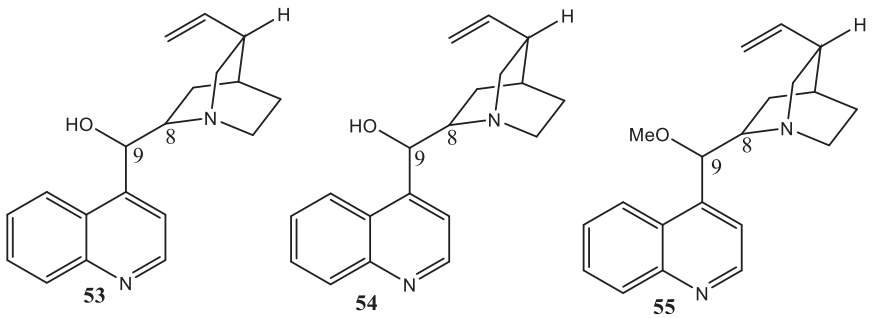


Scheme 13 Diastereoselective synthesis of furocoumarin derivatives.



Scheme 14 Hydrogenation of an aliphatic α-ketoester.

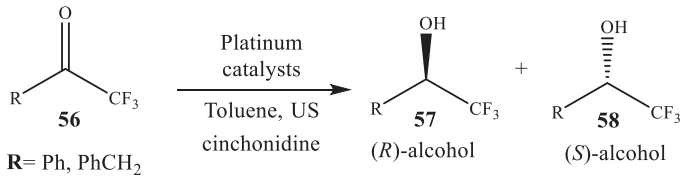
Further, Bartok and coworkers [37] described enantioselective hydrogenation of different α-ketoester to hydroxy derivatives under sonication using platinum catalysts Pt/Al_2O_3 modified by cinchona. Different kinds of cinchona such as cinchonidine **53**, cinchonine **54,** and 9-*O*-methoxy-10,11-dihydro cinchonidine **55** were used as a modifier (Scheme 15) and best results were found with cinchonine. Because chiral sites of modifiers are increased by ultrasonication, the rate of reaction also increased.



Scheme 15 Different type of cinchona derivatives.

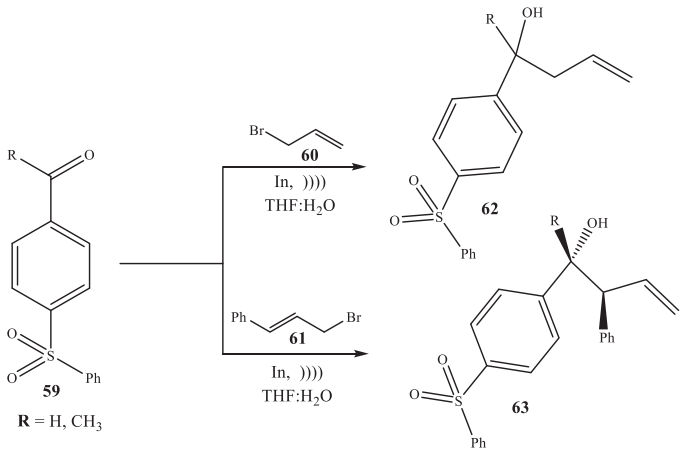
Same chemo- and enantioselective reaction was also reported by Torok and coworkers [38] using platinum catalyst modified by cinchonidine under ultrasonic irradiation.

Bartok and coworkers [39] reported enantioselective hydrogenation of prochiral α,α,α-trifluoromethyl ketones **56** to (*R*)-alcohols **57** and (*S*)-alcohols **58** under sonication using platinum catalysts modified by cinchonidine (Scheme 16). They used different platinum catalysts such as Pt/C, Pt/SiO_2, Pt/Al_2O_3, and Pt/K-10 but reaction proceeded faster with Pt/Al_2O_3 catalyst under ultrasonication. They also used these catalysts under conventional heating but it took longer reaction time to completion. Further, they tried different solvents such as toluene, DCB, acetic acid but higher ee (enantiomeric excess) values obtained in DCB. The enantioselectivity and yield were improved by insonation of the catalyst in both aerobic and anaerobic conditions.



Scheme 16 Enantioselective synthesis of (*R*)-alcohols and (*S*)-alcohols by hydrogenation.

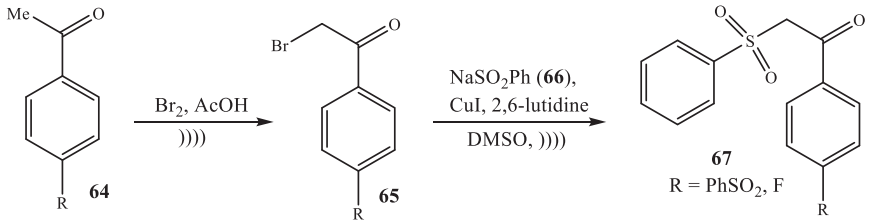
Jørgensen and coworkers [40] have developed a methodology for Barbier-type reaction under ultrasonication for the synthesis of regio- and diastereoselective homoallylic alcohols **62,63** incorporating sulfone moieties with antiselectivity, by the reaction of diverse carbonyl compounds **59** with allylic bromides **60** using water as reaction medium catalyzed by indium (Scheme 17). Initially, reaction tried at room temperature, but no product formation has taken place after days but as temperature increased to 50°C, the product obtained in excellent yield after longer reaction time (12 h). Further, they transferred this reaction into sonication and product obtained with excellent yield in 3 h. To check the diastereoselectivity of the reaction, used cinnamyl bromide **61** and obtained only γ-adduct as the product with antiselectivity. Mechanistically, the product formation has taken place by six-membered cyclic structure with a large group at equatorial position



Scheme 17 Synthesis of homoallylic alcohols incorporating sulfone moieties.

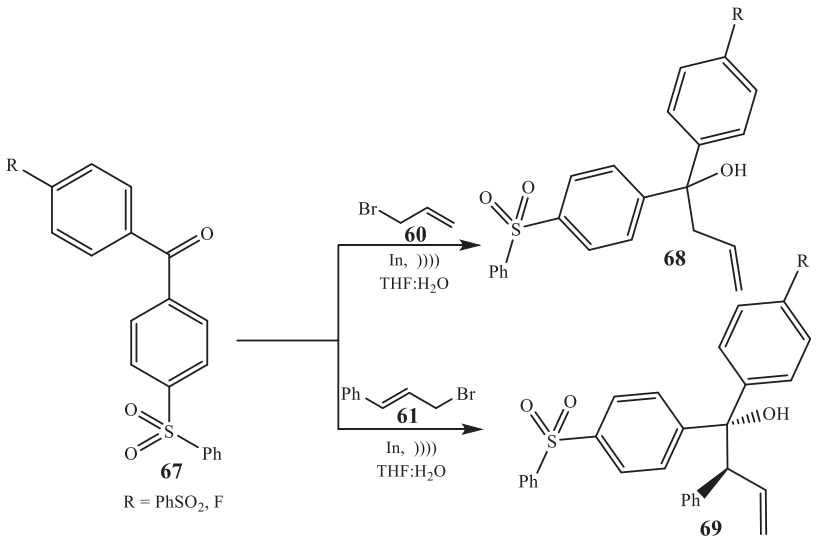
Further, they introduced substituted aryl ketones to check the selectivity for the synthesis of homoallylic alcohols incorporating sulfone moieties. In this context, they synthesized substituted α-bromoacetophenones **65** by the bromination reaction of substituted acetophenones **64** under sonication using acetic acid as solvent. Further, carbonyl compounds having sulfone moiety **67** at para position were synthesized by the

reaction of sodium benzenesulfinate **66** in the presence of cuprous iodide and 2,6-lutidine under ultrasonication using DMSO as solvent (Scheme 18). 2,6-Lutidine is a weak and sterically hindered base but with CuI, it behaves as the superior base.



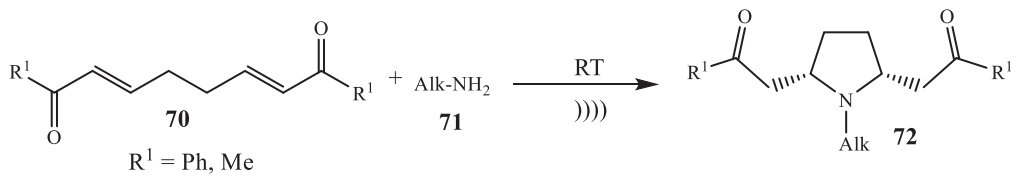
Scheme 18 Synthesis of aryl ketones having sulfone moiety.

Further, allylation reaction carried out under the same reaction conditions such as water as reaction medium and indium as the catalyst, with allyl **60** and cinnamyl bromides **61** and homoallylic alcohols **68,69** were obtained with good stereoselectivity, i.e., anti-selectivity (Scheme 19).



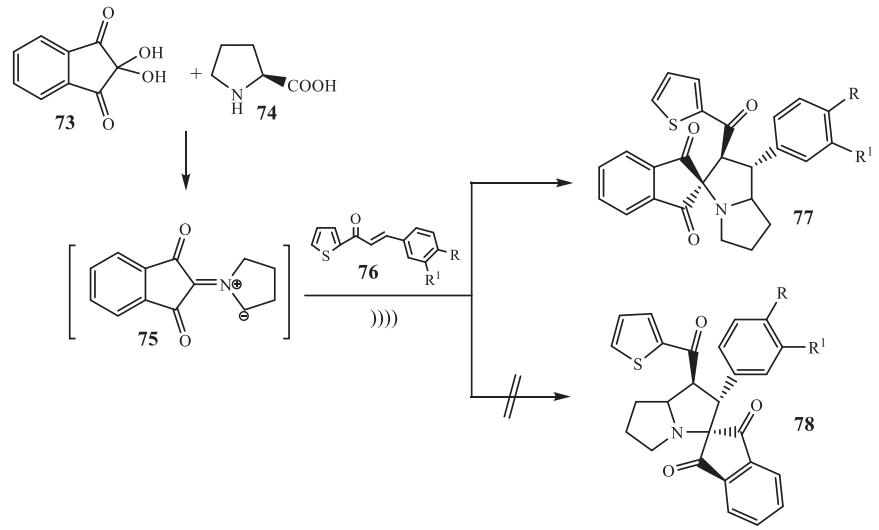
Scheme 19 Synthesis of homoallylic alcohols with antiselectivity.

Joseph and coworkers [41] have been synthesized 2,5-meso-pyrrolidines **72** using aza-Michael addition reaction of bis-enones **70** and primary alkylamines **71** under ultrasonication and this method showed high stereoselectivity (Scheme 20). They tried many solvents but under ultrasonication, solvent is not required.



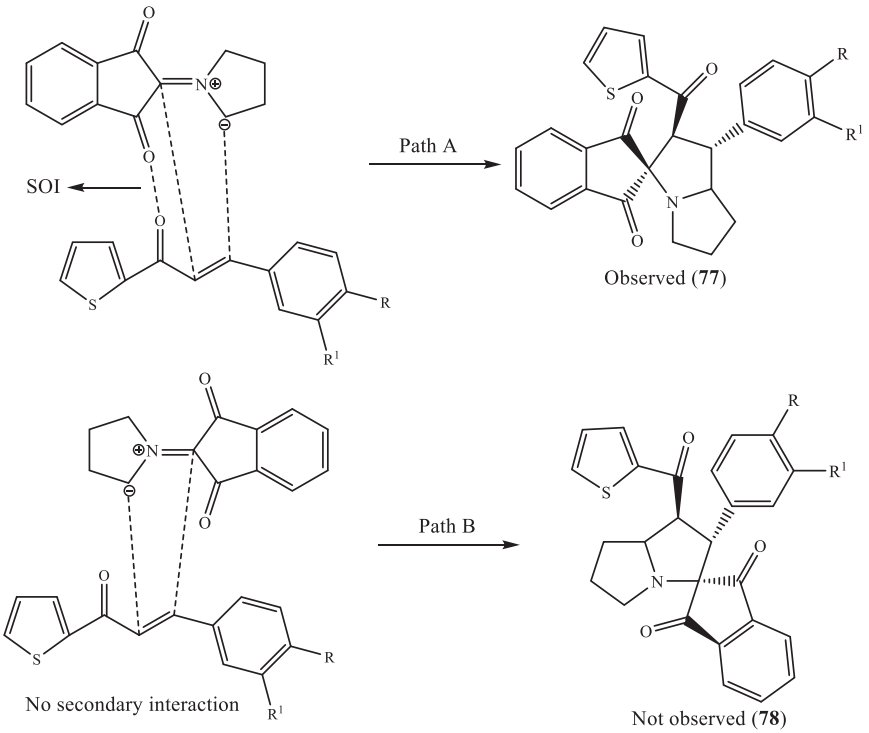
Scheme 20 Synthesis of pyrrolidines.

Spiroindanedione pyrrolizidine derivatives **77** were synthesized by Valliappan and coworkers [42] under ultrasonication. The stereoselective preparation of spiro compound was done by the 1,3-dipolar cycloaddition reaction of (*E*)-3-aryl-1-(thiophen-2-yl)prop-2-en-1-ones **76** with azomethine ylides **75**. Azomethine ylides were obtained during the reaction of ninhydrin **73** with L-proline **74** (Scheme 21). Initially, reaction of ninhydrin **73**, L-proline **74**, and (*E*)-3-aryl-1-(thiophen-2-yl)prop-2-en-1-ones **76** was carried out under conventional heating using methanol as a solvent but took longer time to completion with lower yield but under ultrasonication gave excellent yield with shorter reaction time.



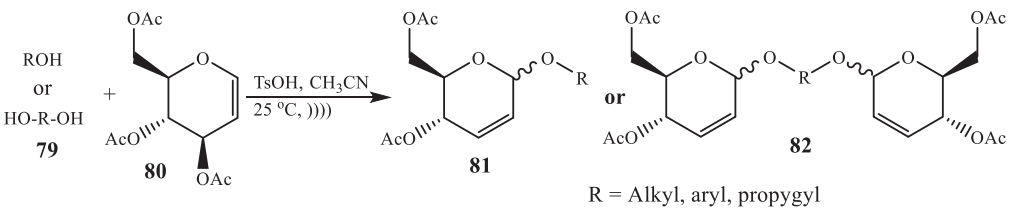
Scheme 21 Synthesis of spiroindanedionepyrrolizidine derivatives.

Mechanistically, the reaction proceeded through path **A** because secondary orbital interaction (SOI) was found between carbonyl group of (*E*)-3-aryl-1-(thiophen-2-yl) prop-2-en-1-ones and azomethine ylides which is not possible in path **B** (Scheme 22).



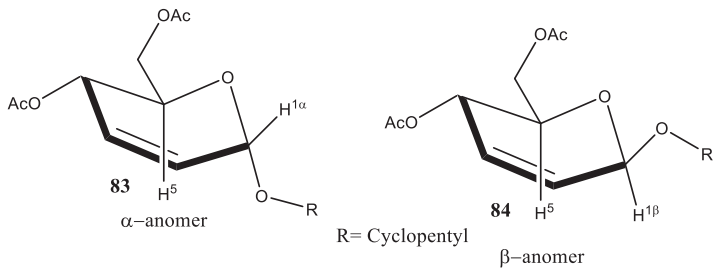
Scheme 22 Showing secondary orbital interaction (SOI).

Freitas and coworkers [43] developed a methodology for the glycosidation of alcohols **79** with 3,4,6-tri-*O*-acetyl-D-glucal **80** using acetonitrile as a solvent under ultrasonic irradiation (Scheme 23). Initially, reaction tried without catalyst but no product obtained. After this, they used a different kind of additives such as amberlyst A-15, montmorillonites K10, KSF but no product formed. Further, TsOH was used as additive and product obtained in excellent yield within 5 min of irradiation.



Scheme 23 Glycosidation of alcohols.

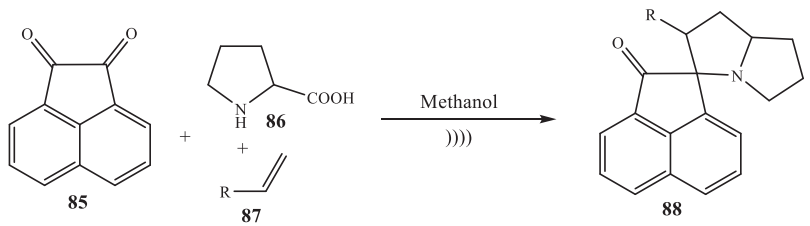
The stereochemistry of products determined by proton NMR spectroscopy (NOESY). According to proton NMR, there is the formation of two anomers, i.e., α-anomer **83** and β-anomer **84**. The H^1 and H^5 protons of α-anomer have opposite stereochemistry while β-anomer produced a positive NOE effect which indicates that α-anomer was found as the major product (Scheme 24).



Scheme 24 Stereochemistry of the product.

Further, they successfully employed this methodology for the glycosidation of hindered and non-hindered, cyclic, acyclic, allylic, homoallylic, benzylic alcohols, and phenols with α-anomeric selectivity. Furthermore, rigid or flexible glycols were also successfully used for the glycosidation reaction under ultrasonic irradiation.

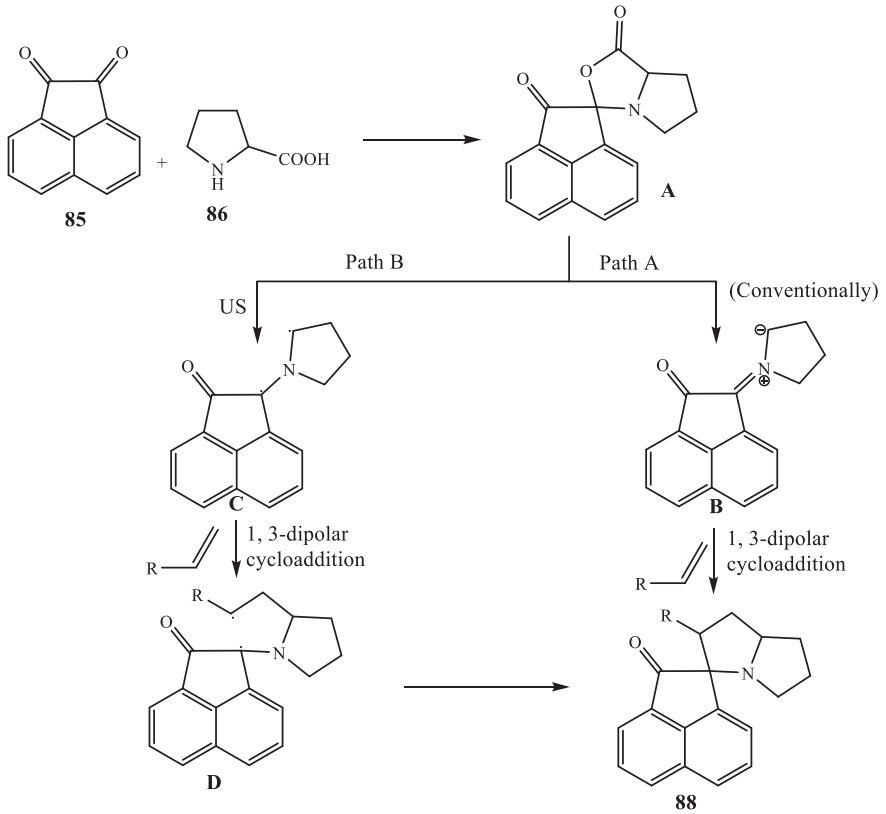
Spiro pyrrolizidines **88** were synthesized by Jadidi and coworkers [44] by the reaction of acenaphthoquinone **85**, proline **86,** and various substituted alkenes (as dipolarophiles) **87** under ultrasonication using methanol as solvent (Scheme 25). Spiro pyrrolizidines were obtained via 1, 3-dipolar cycloaddition of dipolarophiles with azomethine ylides which was produced during the reaction from acenaphthoquinone and proline.



Scheme 25 Synthesis of spiro pyrrolizidine derivatives.

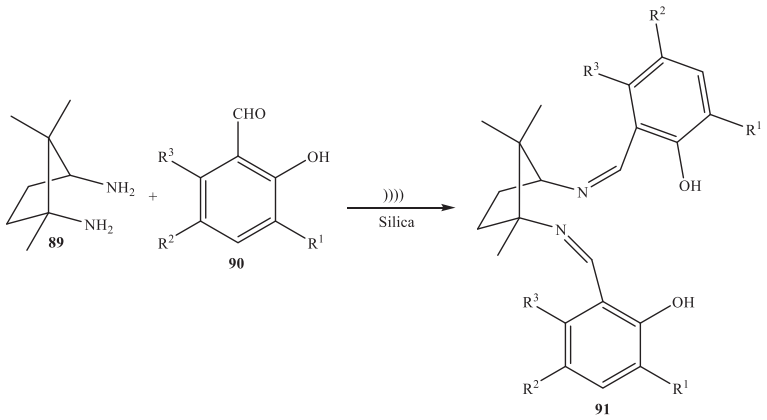
Mechanistically, acenaphthoquinone **85** and proline **86** formed intermediate **A** which decarboxylated by heat to formed azomethine ylide B and under ultrasonic irradiation formed diradical **C** which subsequently gave [3 + 2] cycloaddition reaction with alkenes 87 to afford final product **88** (Scheme 26). Spiro pyrrolizidines have three stereogenic centers which means that there is the possibility of formation of eight different

diastereomers but only a single product obtained. Further, they also checked the possibility of a biradical mechanism using *p*-benzoquinone as a radical scavenger, hence it slows down the rate of reaction in the presence of *p*-benzoquinone which proved that the reaction also follows the radical mechanism under ultrasonication.



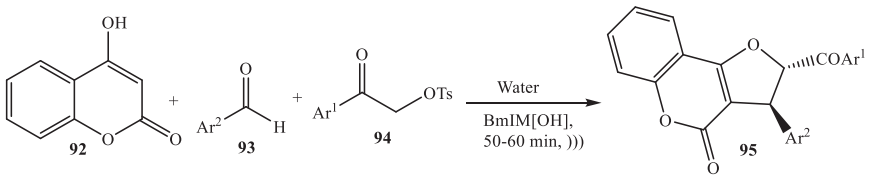
Scheme 26 Plausible mechanism for the synthesis of spiro pyrrolizidines.

Serra and coworkers [45] have developed a pathway for the synthesis of chiral salen ligands **91** by the reaction of (*1R,3S*)-diaminocyclopentane derivatives **89** with hydroxybenzaldehydes **90** under ultrasonication (Scheme 27). Initially, the reaction of the diamine with the aldehydes was carried out in ethanol but reaction took longer time to completion with a lower yield. Further, they tried the reaction of diamine (*1R, 3S*) with 2 equivalents of salicylaldehyde underneath ultrasonication using silica as a promoter and found complete conversion with good yield within shorten reaction time. After the synthesis of chiral salen ligands **91** used in the enantioselective synthesis of trimethylsilylcyanation of benzaldehyde.



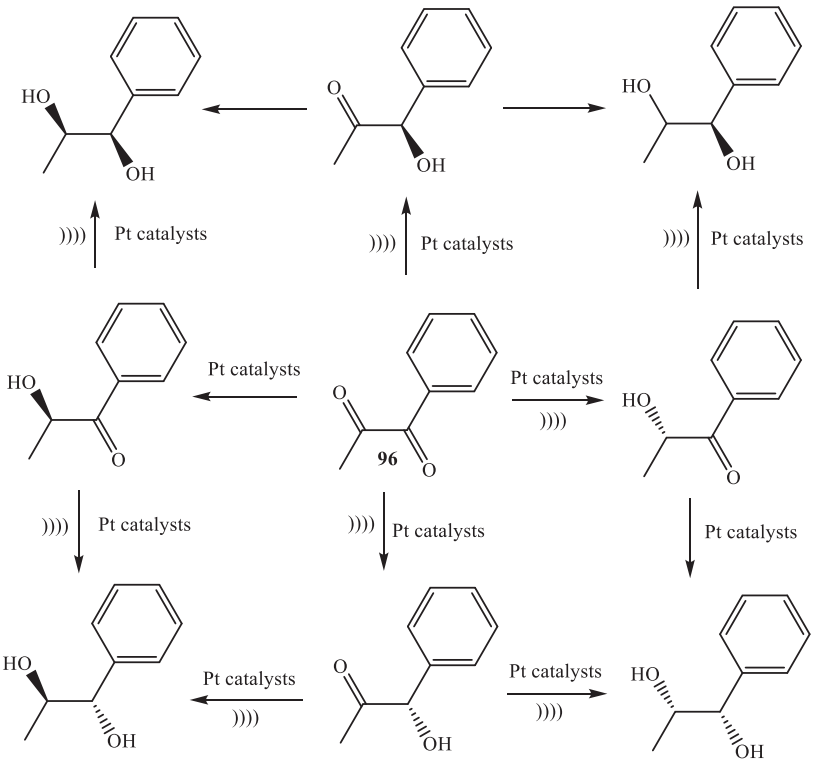
Scheme 27 Synthesis of chiral salen ligands.

Wadhwa and coworkers [46] have been developed a pathway for the diastereoselective synthesis of trans dihydrofuro coumarin derivatives **95** by the reaction of 4-hydroxy coumarin **92**, aldehydes **93**, and α-tosyloxyketones **94** under ultrasonication using water as solvent and [BMIm]OH ionic liquid as catalyst (Scheme 28). Initially, the different catalyst was used such as piperidine, $NahCO_3$, DBU, NaOH, imidazole, and [BMIm]OH ionic liquid but the best result was found in 30 mol% [BMIm]OH ionic liquid. Proton NMR study showed that two protons at 2,3-position of the dihydrofuran (DHF) were in the opposite direction to each other, i.e., trans stereochemistry of the product.



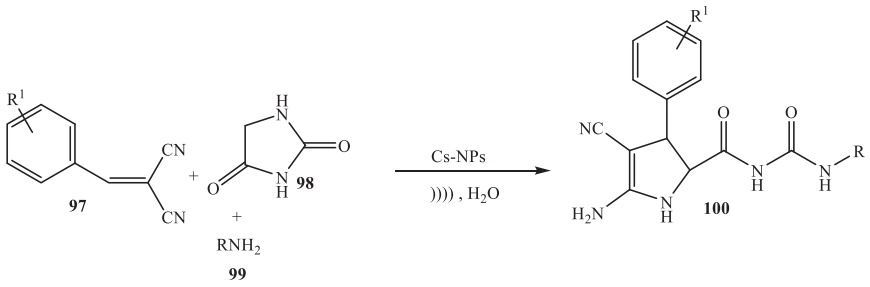
Scheme 28 Synthesis of trans dihydrofuro coumarin derivatives.

Murzin and coworkers [47] have used a different kind of platinum catalysts such as Pt/Al_2O_3, Pt/SiO_2, Pt/SF, and Pt/C cinchonidine for the enantioselective hydrogenation of diketone **96** under ultrasonication (Scheme 29). Initially, reaction tried using Pt/SF (Silica fiber) and an increase in the rate of reaction with the enhancement of enantiomeric excess was found compared to without catalyst conditions. Further, other catalysts were successfully employed and found that Pt/Al_2O_3 was the best catalyst for enantioselective hydrogenation of diketone in terms of highest regioselectivity (rs) and enantiomeric excess (ee).



Scheme 29 Enantioselective hydrogenation of diketone.

Ghomi and coworkers [48] were prepared chitosan nanoparticles (CS-NPs) and used as a catalyst in the diastereoselective synthesis of dihydropyrroles **100** using one-pot reaction of 2-arylidene malononitrile **97**, hydantoin **98,** and amines **99** under ultrasonication using water as solvent (Scheme 30). To check the catalytic role of chitosan nanoparticles, they tried reaction without catalyst but no product was obtained after longer reaction time. Further, a catalytic amount of 0.02 g of chitosan nanoparticles was used in aqueous



Scheme 30 Diastereoselective synthesis of dihydropyrrole derivatives.

medium and dihydropyrroles obtained with high diastereoselectivity. The stereochemistry of product determined by ^{1}H-^{1}H NOESY spectra (small NOE effects) which showed that two hydrogen atoms at second and third position of pyrrole ring were opposite to each other, i.e., trans stereochemistry of the product.

3. Conclusion

It is hoped that this chapter has given the idea about the use of ultrasound in stereoselective organic synthesis. Many stereoselective reactions were successfully employed under ultrasonic irradiation which was not possible under conventional heating. Sonochemical reactions have many advantages such as no side product formation, easier separation process, cleaner reaction pathways, and many more. Selectivity plays a big role in the synthesis of medicinally important compounds and many drugs. We hope and anticipate that this chapter will offer further information to the reader for the use of ultrasonic chemistry in stereoselective organic synthesis.

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CHAPTER 4

Sonochemical protocol for alkylation reactions

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1. Introduction

The ultrasound activation is based on the phenomenon of cavitation including formation, growth, and collapse of vapor bubbles in a liquid solution to contribute the energy for conducting the organic synthesis [1–4]. The principle of sonochemistry is cavitation provided high temperature and pressure by the collapsing bubble in liquid under ultrasound reaching thousands of degrees Kelvin and several hundred atmospheres which can enhance a wide range of chemical processes [5]. This region with high temperature and pressure is defined the "hot spot" generated under ultrasound irradiation [6, 7]. Recently, the ultrasound irradiation has been received with much attention in many fields including organic transformation [2, 7–9], preparation of nanoscale metal-organic coordination polymers [10, 11], catalysis [12], enzyme activation [4, 6], synthesis of zeolite [13], preparation of metal-organic framework [14], and graphene synthesis [15].

Alkylation reactions have been known as essential tools in organic synthesis, which is the couplings between a nucleophile and an alkylating reagent to form C—C bond-forming reaction. Herein, the chapter focuses on ultrasound-assisted various alkylation reactions, including *C*-, *N*-, *O*-, and *S*-alkylation.

2. Alkylation reaction

In 1887, Charles Friedel and James Mason Crafts reported the successful preparation of amylbenzene for the reaction of amyl chloride and benzene in the presence of $AlCl_3$, and it was the first example of alkylation [16]. Up to now, Friedel-Crafts alkylations have been the best method for the alkylation of aromatic compounds [17, 18]. The traditional protocol that employed the homogeneous catalysts including BF_3, $AlCl_3$, $TiCl_4$, $NbCl_5$, $SbCl_5$, or $SnCl_4$ suffered from several drawbacks such as the excess of catalyst loading, prolonged reaction time, polyalkylation, low yield, and difficult recovery of catalyst [19, 20]. Therefore, heterogeneous catalysts are useful alternatives due to easier setup and workup. Some of the solid catalysts such as sulfated zirconia [21], Fe-doped $HTaWO_6$ nanotubes [22], a Bronsted-acidic ionic liquid gel, metal-organic frameworks [23, 24],

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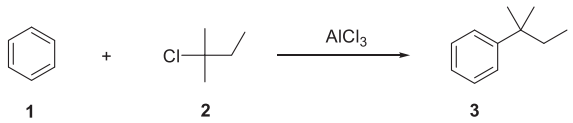
https://doi.org/10.1016/B978-0-12-819540-6.00004-8

and iron-modified mesoporous silica have been developed [25]. Due to great interest in Friedel-Crafts alkylation, many different protocols have been developed for the reaction. With the demand for more environmentally and economically benign processes, ultrasound activation-assisted alkylation reaction displays beneficial effects on the reactions because it could enhance the reaction rate, reduce the reaction time, and improve the product selectivity. The use of ultrasound irradiation provides the green activator for organic synthesis catalyzed by both homogeneous and heterogeneous catalysts due to high temperature and pressure pulse in the cavitation phenomenon (Scheme 1).

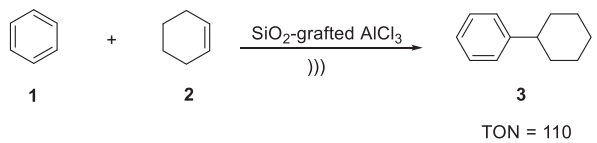


Scheme 1 The *C*-alkylation reaction catalyzed by $AlCl_3$.

3. Alkylation reaction under sonication

3.1 *C*-Alkylation reaction

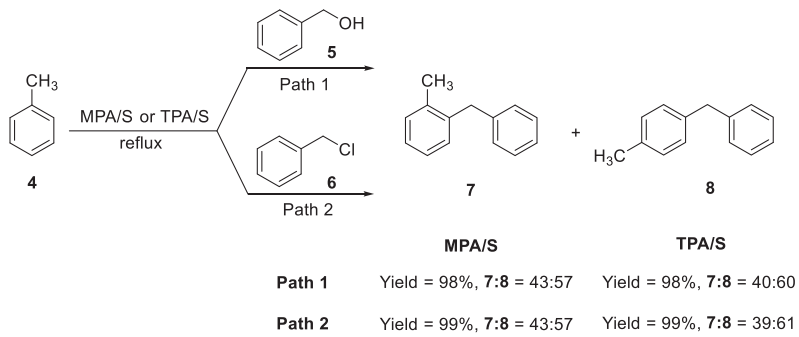
The alkylation of benzenes with olefins by catalyzed by Lewis acids has been reported in low yields due to the generation of by-product such as resinous substances. The catalytic activity of SiO_2@$AlCl_3$ was tested on the alkylation between benzene and cyclohexene under ultrasonic vibration by Sato [26]. The catalyst was highly active at 0°C and the value of TON attained 110 (according to report: TON was calculated by mol of the product based on mol of Al atom in the catalyst). Under ultrasound activation, the speed of reaction was significant accelerating, the cause of the accelerating was the improvement of mass transfer of reactants and product. In addition, the catalytic supports are convenient to be recovered and reused for the catalytic reaction, and it is secure handling. However, in this case, the SiO_2@A1C1$_3$ activities were gradually decreased in catalytic activity by the repetition of the catalytic runs (Scheme 2).



Scheme 2 The alkylation reaction catalyzed by SiO_2-grafted $AlCl_3$ under ultrasound irradiation.

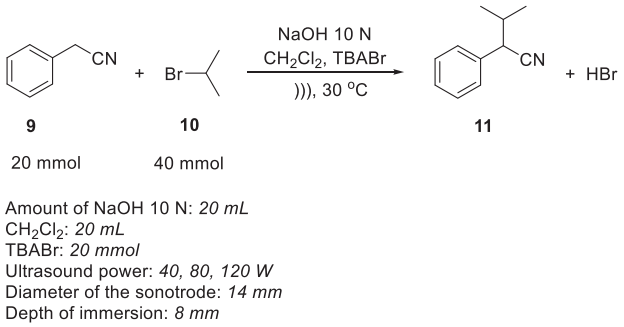
Ultrasound-assisted silica-supported Keggin heteropolyacids was reported by Pizzio and coworker [27]. Molybphosphoric and tungstophosphoric acids supported on silica (MPA/S and TPA/S, respectively) were investigated as the catalysts for aromatic alkylation reactions. The alkylation reagents including benzyl alcohol, benzyl chloride,

cyclohexene, and cyclohexanol were used to alkylation of benzene and toluene in the presence of these heterogeneous catalysts. The reactions were performed under conventional heating and ultrasound irradiation, which allowed quantitative conversions in short times; the monoalkylation products were afforded in excellent yields (Scheme 3).



Scheme 3 The aromatic alkylation reactions catalyzed by MPA/S or TPA/S.

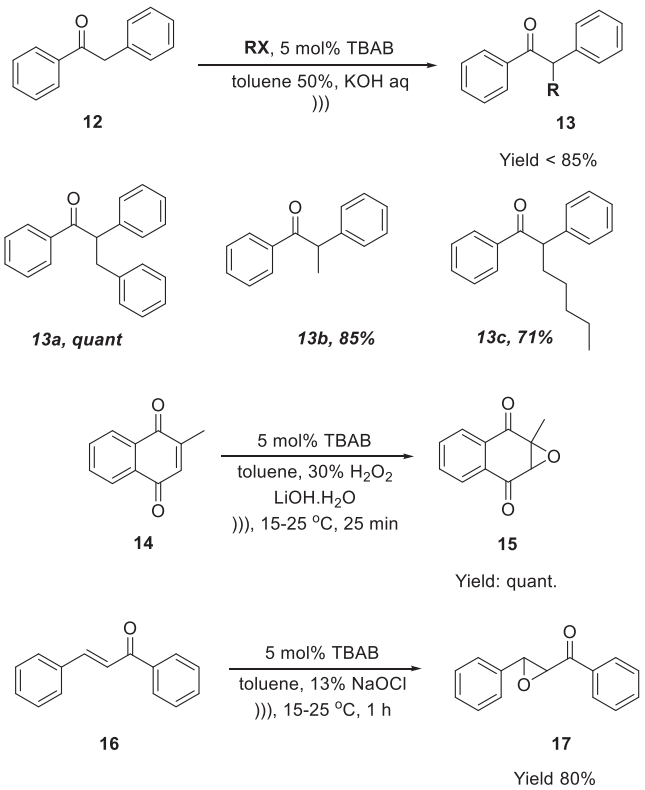
Quaternary ammonium salts were used in the *C*-alkylation reaction of benzyl cyanide with 2-bromopropane and sodium hydroxide under sonication [28]. 3-Methyl-2-phenylbutyronitrile was attained in high yield under room-temperature sonication. The reaction rate could be improved under ultrasound activation, but the frequency of ultrasonic and the geometry of the field affect strongly to the reaction rate. It means that a good efficiency of ultrasound in the reaction mixture was obtained when the ultrasound and geometry of the sonotrode had to be adopted (Scheme 4).



Scheme 4 The *C*-alkylation reaction using NaOH under sonication.

Next, Ooi and coworkers demonstrated the alkylation reaction of *tert*-butyl glycinate-benzophenone Schiff base using phase-transfer catalyst under sonication [29]. The reaction of 2-methyl-1,4-naphthoquinone and tetrabutylammonium bromide

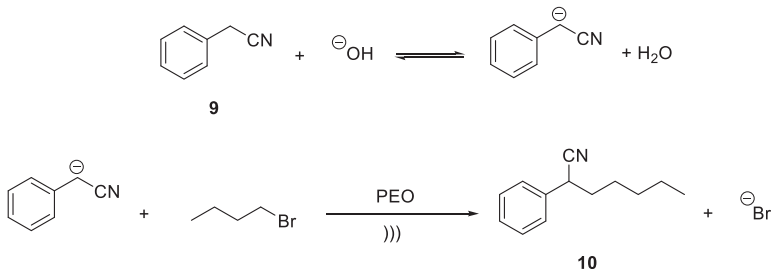
(5 mol%) in the presence of toluene with 30% H_2O_2 aqueous and $LiOH.H_2O$ was tested at 15–25°C for 25 min. The similar condition, the epoxidation of *trans*-chalcone was carried out in the presence of 13% NaOCl. The mixture of *tert*-butyl glycinate-benzophenone Schiff, methyl iodide and quaternary ammonium salt (1 mol%) in toluene and 50% KOH solution was activated under ultrasound at 0°C for 1 h provided a higher yield of the corresponding product and the enantiomeric selectivity was obtained in 88% ee. The yield and selectivity were compared with a reaction carried out under magnetic stirring at 0°C for 8 h (64%, 90% ee). The results showed that the desired product was gained in high selectivity and conversion under ultrasound irradiation (Scheme 5).



Scheme 5 The ultrasonic irradiation-assisted liquid-liquid phase-transfer catalyst for alkylation reactions.

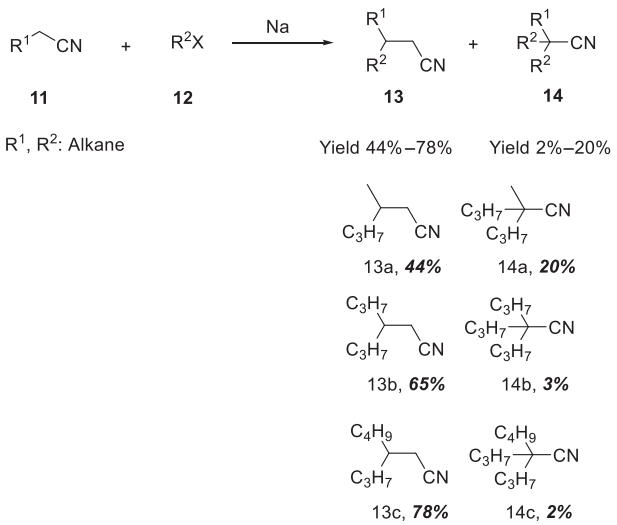
Tsanov's group used the gel of cross-linked poly(ethylene oxide) (PEO) as an efficient the phase-transfer catalysis in the alkylation of phenylacetonitrile and 1-bromobutane in the presence of hydroxide base under sonication [30]. The ultrasound enhanced the mixing of the organic phase, and potassium hydroxide proceeded in the increased alkylation rate. The high yield was observed under ultrasound activation and the modified with

poly(ethyleneimine) PEO showed the highest catalytic activity in the same reaction. The phase-transfer catalyst could be reused several times without significant decrease in the catalytic activity (Scheme 6).



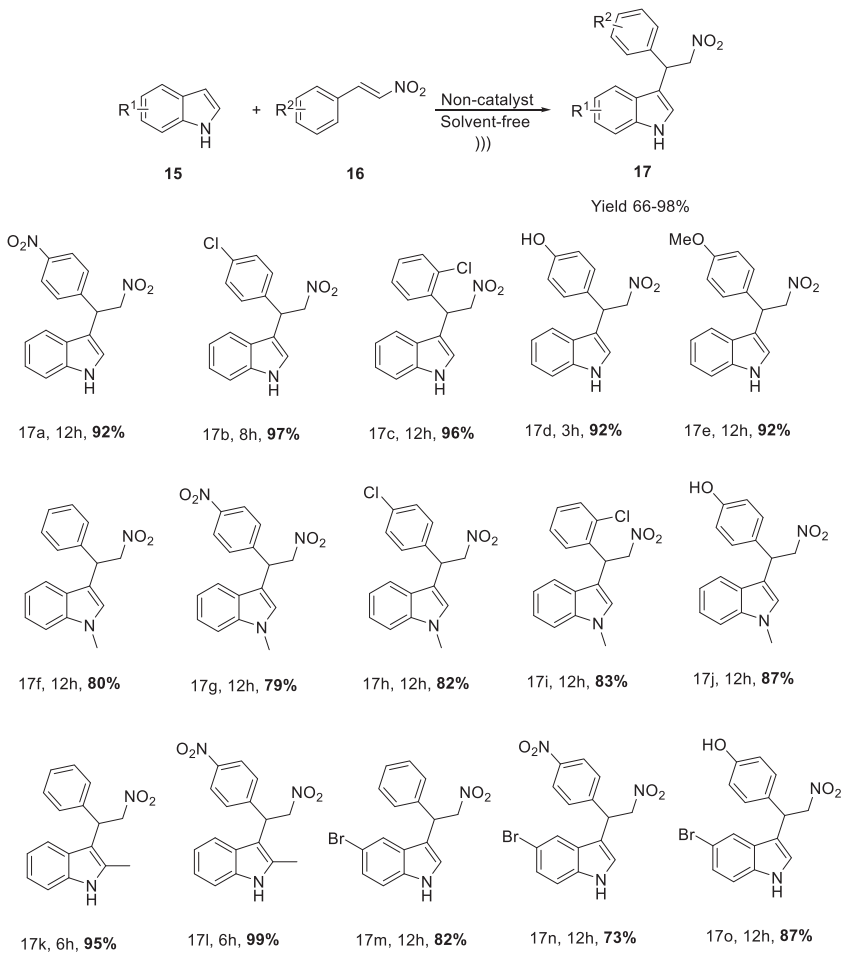
Scheme 6 The alkylation reaction of phenylacetonitrile with 1-bromobutane in the presence of KOH.

Berlan and coworkers described the deprotonation and alkylation of *n*-alkyl cyanides and an alkyl halide with sodium under sonochemical conditions [31]. The reaction competed favorably in terms of yield and work up. Comparative experiments displayed that under stirring, the yields and selectivity were poorer. In addition, it is crucial to emphasis an exciting detection when results of the same type are observed with a high-speed stirrer (9000 rpm). The sonication is known to increase cavitation, the reactor used here provides a cavitating power wave of 2.7 kHz frequency, which demonstrates the influence of frequency on sonochemical processes (Scheme 7).



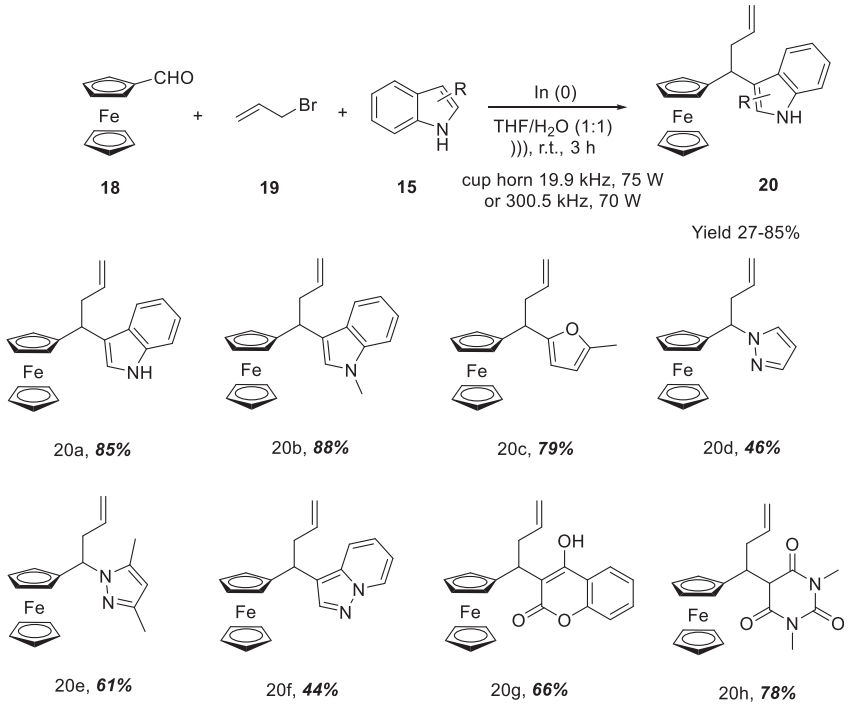
Scheme 7 The deprotonation-alkylation of alkyl cyanides under sonication.

Fu and Shao reported the preparation of 3-substituted indole derivatives from the reaction of indoles and nitroalkenes under solvent-free sonication [32]. The experiments were performed with 2-chloroethanol as a mild acidic promoter of the procedure. The selectivity of the product was controlled at the C3 position of indoles after over 3–12 h in the absence of solvent and catalysis. These findings showed that the ultrasound irradiation could increase the reactivity of the reagents, and 2-chloroethanol was an efficient promoter for the reaction. Interestingly, the current method could be applied on a large scale with only 5 mol% 2-chloroethanol to provide the desired product in a yield of 93% and excellent selectivity. The prominent features of the method are equimolar substrates, high yields, environmentally benign conditions, simplicity of workup (Scheme 8).



Scheme 8 The synthesis of 3-substituted indole from indoles and nitroalkenes under sonication.

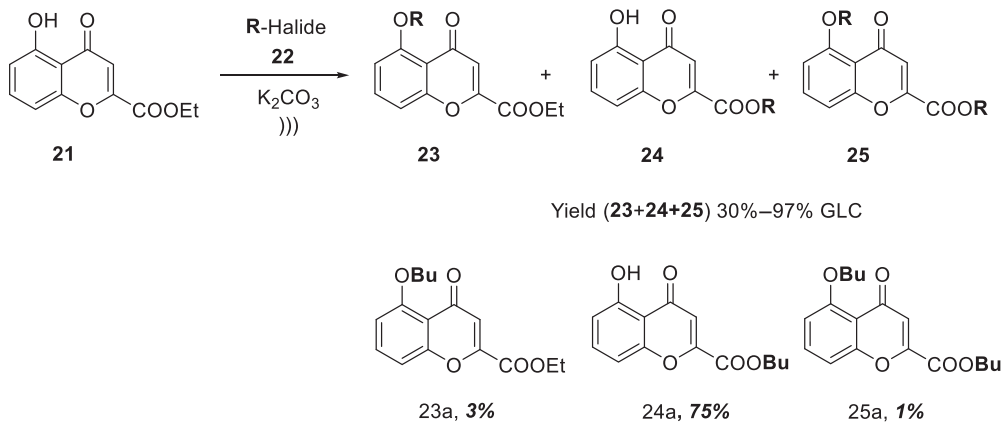
Cappelletti's group disclosed the ultrasonic-assisted one-pot domino reaction with ferrocenecarboxaldehyde [33]. Ultrasound irradiation played an important role for the one-pot domino allylindation-dehydrative alkylation reaction of ferrocenecarboxaldehyde. The *C*-nucleophiles reaction was carried out with electron-rich (hetero)arenes in THF/H_2O (volume = 1:1). Ultrasound activation performed in three reactors: a bath (20.3 kHz, 60 W), a cup horn (19.9 kHz, 75 W), and another cup horn (300.5 kHz, 70 W) affording 18 new ferrocenyl derivatives in good to excellent yields (Scheme 9).



Scheme 9 The allylindation and dehydrative alkylation reactions through the one-pot domino reaction.

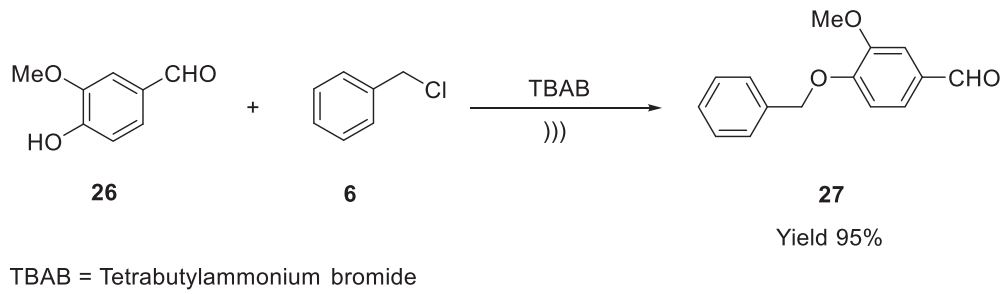
3.2 *O*-Alkylation reaction

Mason's group reported the *O*-alkylation of phenol using potassium carbonate (K_2CO_3) in the presence of solvents such as acetone and butan-2-one, which has previously been synthesizing of alkoxy benzenes [34]. The reaction can be improved by using phase transfer catalysis without solvents or using the power ultrasound in the presence of a polar aprotic solvent such as *N*-methylpyrolidinone. Ultrasound irradiation assisted the a1kylation of the 5-hydroxychromone with 1-bromobutane in *N*-methyl pyrrolidinone enhances the reaction yield and selectivity. Besides, ultrasound irradiation could enhance the formation of the further reaction of the *O*-alkylated product with the excess 1-bromobutane (Scheme 10).



Scheme 10 The *O*-alkylation of 5-hydroxychromones under ultrasound irradiation.

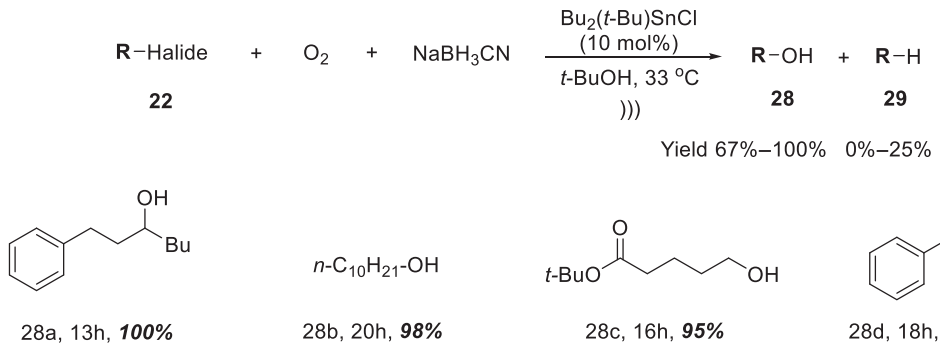
Dubey and Gogate reported the synthesis of 4-benzyloxy-3-methoxybenzaldehyde via the O-alkylation reaction of vanillin and benzyl chloride catalyzed by tetrabutylammonium bromide as a phase transfer catalyst under ultrasonic irradiation [35]. The experiments were carried out in a 150-mL vessel joined with a condenser under ultrasound irradiation (using an ultrasonic horn 20 kHz, 120 W). The effects of reaction conditions including temperature, the quantum of an aqueous phase, catalytic amount, molar ratio, and ultrasonic power have been screened, and kinetic studies have also been investigated. Notably, the yield of the desired product was higher under ultrasound irradiation as compared to conventional heating (Scheme 11).



Scheme 11 The selective *O*-alkylation of vanillin with benzyl chloride.

Sawamura and coworkers reported the transformation of alkyl halides to alcohols in the presence of trialkyltin halide/$NaBH_3CN$ system *via* an aerobic radical reaction under sonochemical conditions provided the expected product in high yield [36]. The method proved that the ultrasound activation played an essential role in radical initiation and assisted the formation of Bu_2(*t*-Bu)SnH. The procedure can be applied for various

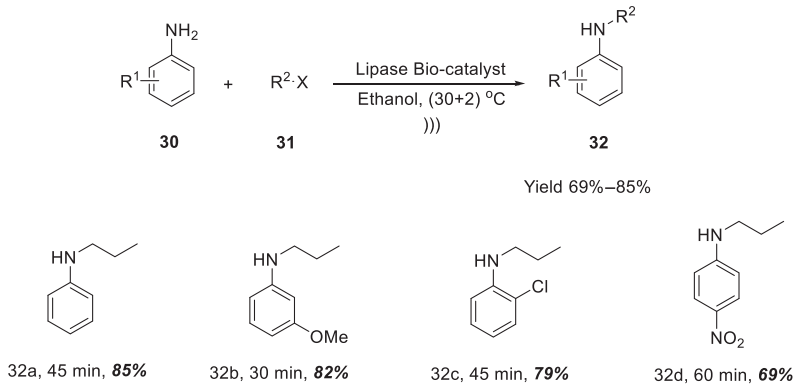
substrates, including alkyl iodide and allylic and benzylic bromide afforded the desired products in good to excellent yields (Scheme 12).



Scheme 12 The synthesis of alcohols from R-halide in the presence of trialkyltin halide/$NaBH_3CN$ system.

3.3 *N*-Alkylation reaction

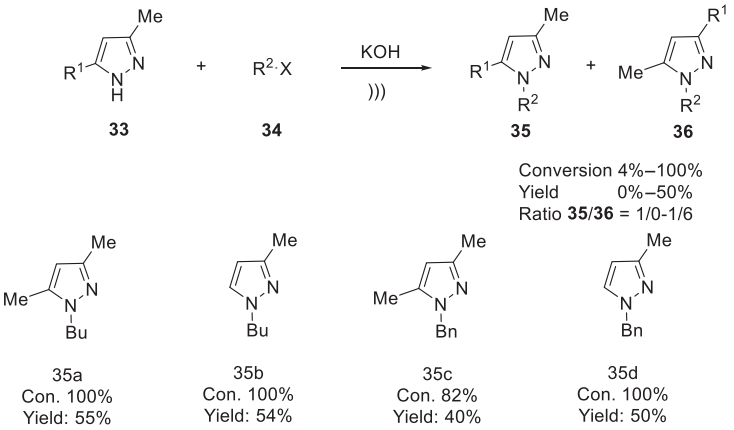
Lobo's group conducted a comparison of using sonochemical and non-sonochemical system for mono-alkylation of primary aromatic amines at elevated temperature and room temperature [37]. The outstanding features of ultrasound are that it allows reducing the reaction time, improving the reaction yield and selectivity. The method is simple, efficient, and environmentally benign. Furthermore, the catalyst and solvent were easily recovered and reused several times and the mono-*N*-alkylation reaction under ultrasound irradiation can be applied to industrial processes (Scheme 13).



Scheme 13 The mono-*N*-alkylation reaction of primary aromatic amines.

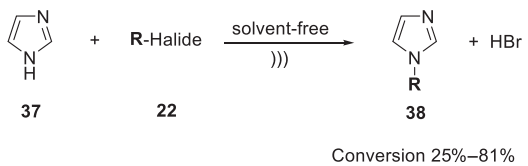
Frizzo and coworkers performed the derivative *N*-alkylation reaction between pyrazoles and alkane halide and KOH in the presence of 25 different solvents such as aprotic

polar solvents, and ionic liquids [38]. Under ultrasound irradiation, the *N*-alkylation of pyrazoles necessitates high temperatures, which occurs according to S_N2 mechanism. The effect of surface tension, viscosity of the solvents, and vapor pressure was tested. The reaction involving acetonitrile mixed with ionic liquids showed faster rate than acetonitrile. Aprotic polar solvents, including DMF, DMSO, and MeCN were investigated in the *N*-alkylation of pyrazoles under ultrasound irradiation. The reagents had been converted into the expected product at 90°C for 5 min. [BMIM][BF_4] was found as the best polar mixing solvent in the current method (Scheme 14).



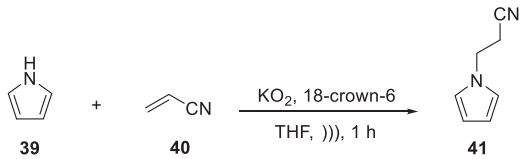
Scheme 14 The *N*-alkylation of pyrazoles under sonication.

Costarrosa and coworkers reported the preparation of *N*-substituted imidazoles through the alkylation of imidazole with 1-bromobutane using alkaline-promoted carbons under sonochemical irradiation [39]. The *N*-alkylation of heterocycles played a vital in the synthesis of catalysis, which was the best way for the preparation of ionic liquids. The sonication enhanced the reagent reactivity such as to accelerate the reaction, to reduce the time reaction, to increase the catalyst efficiency, and to reduce the side product (Scheme 15).



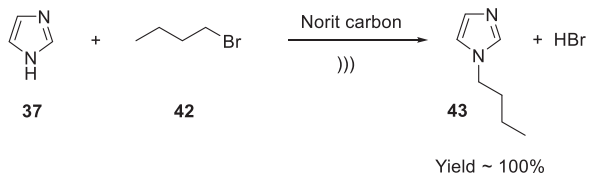
Scheme 15 The *N*-alkylation of imidazole under sonication.

Yim s' group reported the effect of 18-crown-6 in the *N*-alkylation of pyrrole with potassium superoxide as a base under ultrasound irradiation [40]. *N*-alkylating reagents including acrylonitrile allyl cyanide, methyl acrylate methyl iodide, ethyl bromide, and benzyl bromide were investigated. It was shown that the 18-crown-6 assisted the alkylation gave higher yields of desired products than catalyst-free condition in the presence of potassium superoxide as a base. In an extension of the substrate, the alkylation of indole with alkyl amine was tested under ultrasound irradiation and conventional method. The corresponding product was obtained in good yield for 1 h under stirring, and sonication was not essential in the current method (Scheme 16).



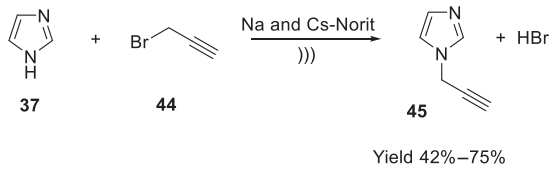
Scheme 16 The *N*-alkylation of pyrrole under sonication.

Ferrera-Escudero and coworker disclosed the preparation of *N*-alkylimidazoles from imidazole and 1-bromobutane with alkaline carbons under ultrasound irradiation [41]. The corresponding products were obtained in high yields and selectivity under the experimental conditions. It is shown that the yield of the product was increased when ultrasound was employed in the alkylation reaction. It is also found that the procedure was enhanced when heterogeneous media was used, the alkaline carbons offer attractive prospects under ultrasound irradiation due to the high yield and mild condition (Scheme 17).



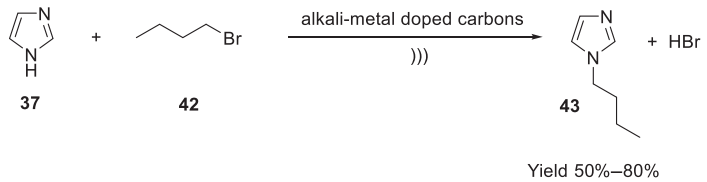
Scheme 17 The synthesis of *N*-alkylimidazole under sonication.

Calvino-Casilda et al. reported the synthesis of *N*-propargyl imidazoles from imidazole with propargyl bromide in the presence of alkaline-doped carbons (Na and Cs-Norit) as heterogeneous catalysts [42]. The *N*-propargyl imidazoles were obtained in high yields when used the Cs^+-Norit carbon as catalyst under solvent-free sonication. The method provides a mild and effective approach for preparation of *N*-propargyl imidazole in good yield and high selectivity. This protocol gives a practical alternative to traditional heating because of its high efficiency and minimal waste (Scheme 18).



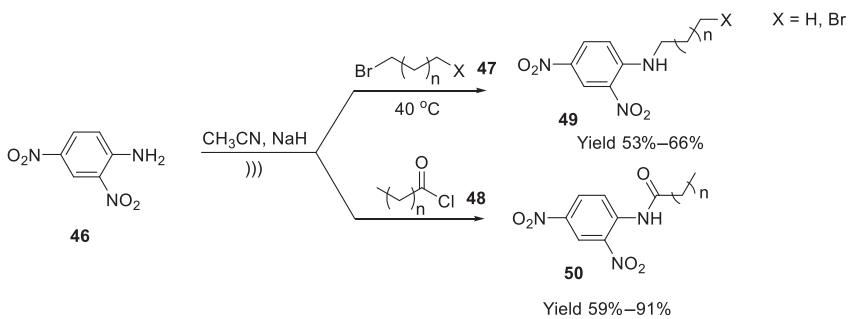
Scheme 18 The synthesis of *N*-propargyl imidazoles under sonication.

López-Pestaña reported the alkylation reaction of *N*-substituted imidazoles of imidazole with 1-bromobutane using two alkali-metal promoted carbons (Na^+- and Cs^+-Norit) as catalysts under sonochemical and thermally activated reactions [43]. *N*-substituted imidazole afforded 80% yield of the desired product and 100% selectivity under solvent-free ultrasound irradiation. The basicity of the alkali metal cation enhances the reaction rate, and ultrasound irradiation is the best choice to increase the yield of the reaction (Scheme 19).



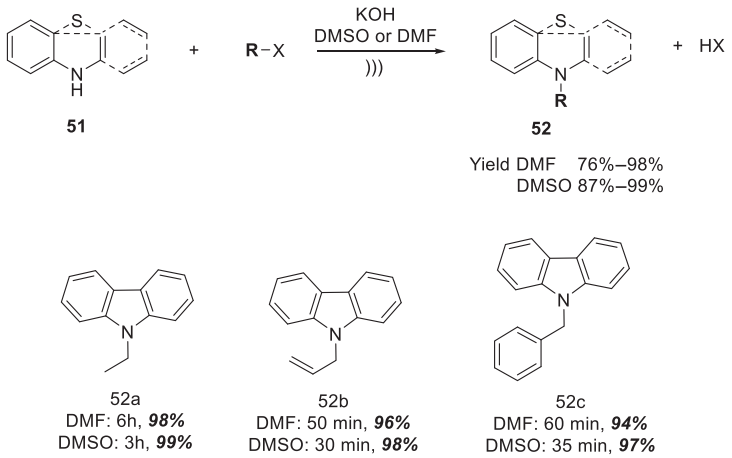
Scheme 19 The synthesis of *N*-substituted imidazoles using alkali-metal doped carbons under sonication.

Khalaj and coworkers investigated the alkylation of amines with alkyl bromides in acetonitrile and sodium hydride under ultrasound activation [44]. The experimental reaction was carried out in a short time and the expected products were obtained in high yields. The method became a good way for the preparation of *N*-alkyl-2,4-dinitrophenylamines and 1-alkoxy-2-alkylbenzimidazoles due to high conversion, cheap and readily available starting materials, and mild reaction conditions (Scheme 20).



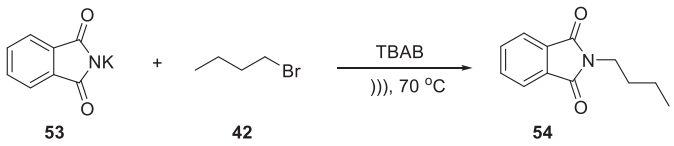
Scheme 20 The *N*-alkylation and *N*-acylation of 2,4-dinitrophenylamine under sonication.

Zhao and coworkers reported that *N*-heterocyclic compounds containing indole, carbazole, and phenothiazine could be alkylated easily in DMSO or DMF in the presence of potassium hydroxide as a base under ultrasonic irradiation [45]. Various *N*-substituted heterocyclic derivatives were successfully prepared under ultrasonic irradiation. The current method reduces reaction time compared with traditional heating and provides the expected products in good yields and selectivity (Scheme 21).



Scheme 21 The alkylation of carbazole, indole, and phenothiazine under sonication.

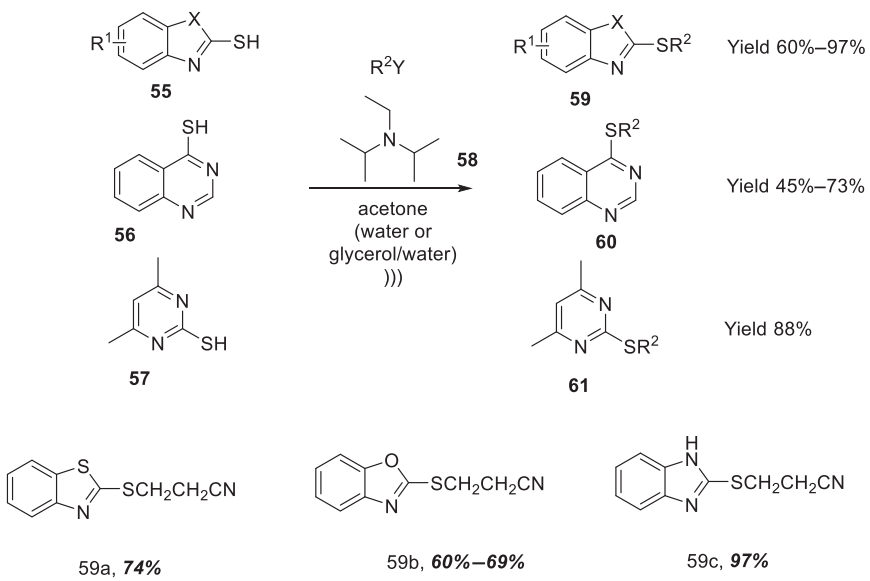
Vivekanand and Maw-Ling reported *N*-butylation of potassium phthalimide with *n*-bromobutane as an alkylating agent in the presence of ultrasonic-assisted phase-transfer catalysis [46]. The synthesis of *N*-butylphthalimide catalyzed by phase-transfer catalysis has improved the yield or enhanced the reaction rate under ultrasound irradiation. The kinetic results displayed a balance between reactants and products, the conversion of *n*-bromobutane equaled the generation of the amount of *N*-butylphthalimide under ultrasonic irradiation. The prominent features of using ultrasound in combination with phase-transfer catalysts are high conversion, short reaction time, good selectivity, and mild reaction conditions (Scheme 22).



Scheme 22 The *N*-alkylation of phthalimide under sonication.

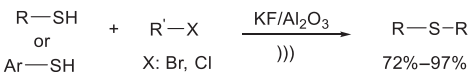
3.4 *S*-Alkylation reaction

Deligeorgiev and coworkers reported the *S*-alkylation of hetaryl thiols with alkyl bromides and alkyl iodides at room temperature under ultrasonic irradiation [47]. The corresponding products have many applications based on their biological activity, which was widely used in the pharmaceutical field such as antifungal, antibacterial, and antitumor activities. The method provided the desired products in good to excellent yields with high purity and in short reaction times (1–30 min) (Scheme 23).



Scheme 23 The *S*-alkylation of hetaryl thiols under sonication.

Nguyen et al. conducted the S-alkylation of thiols with alkyl halide using KF/Al_2O_3 as a solid catalyst under solvent-free ultrasound irradiation, microwave irradiation, and traditional heating [48]. Nine thiols were alkylated with three alkyl halides under solvent-free ultrasound irradiation. The results between *p*-thiocresol and 1-chlorobutane with KF/Al_2O_3 catalyst demonstrated that the yields afforded were 77% after 2 h of ultrasound irradiation and 63% for 5 h of traditional heating. The scope of the reaction was screened under solvent-free sonication and nine sulfides were obtained in good to excellent yields. The activity of KF/Al_2O_3 did not decrease significantly after four consecutive runs (Scheme 24).



Scheme 24 The preparation of thioethers by *S*-alkylation of thiols with alkyl halides under sonication.

4. Conclusions

The prominent features of alkylation reactions in sonication are clean, mild, selective, and efficient for many processes. Ultrasound enhances chemical transformations, mass and heat transfers through cavitational collapse. A variety of alkylation reactions, including *C*, *O*-, *N*-, and *S*-alkylation have been successfully performed under ultrasound irradiation. Ultrasound irradiation allows minimizing the production of waste by improving the yield, selectivity of desired products and reducing the use of organic solvents and hazardous reagents.

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CHAPTER 5

Sonochemical protocol for solvent-free organic synthesis

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1. Introduction

1.1 Ultrasound classification and its applications

Ultrasound irradiation (USI) or ultrasonic rays refer to sound waves in the frequency spectrum of 500 MHz to 20 kHz, which cannot be sensed by the human ear [1]. Ultrasonic rays were discovered in 1883 even years, before X-rays were discovered. The initial application of US was in Great War and were utilized to detect the submarines [2, 3]. However, attributed to its promising physical and chemical influences, currently, US technology is employed for broad range of applications; for instance, wastewater treatment, surface cleaning, phase separation, materials extraction, nano-materials synthesis, food technology, the production of nanoemulsions, electrochemistry, contrast imaging, and therapeutic applications [4–6]. Depending on the application, the US could be divided into two main classes: (i) power ultrasound (20 kHz–2 MHz) or high-intensity ultrasound which is chiefly used in synthesis, emulsifying, de-agglomeration, and liquid mixing [2, 7]; and (ii) low intensity, high frequency ultrasound (above 5 MHz) or diagnostic ultrasound, which is primarily used in nondestructive analysis, noninvasive testing of materials, imaging and medical scanning [2, 8, 9].

1.2 Sonochemistry and its merits

The application of high-intensity ultrasound to accomplish chemical alteration is called as sonochemistry [10]. In sonochemistry, high-intensity and low-frequency (in kHz) US is applied because it alters the medium through which it passes. US has the capability to accelerate or initiate the synthesis of numerous organic targets, by altering the pathway of reaction. Ultrasonic energy has so far merited a broad range of applications in heterogeneous and homogeneous chemistry [11]. Take the field of medicinal chemistry as an example, in which ultrasonic rays are employed to synthesize important biologically active compounds such as ibotenic acid **1**, valdecoxib **2**, isoxazole-4-carboxylic acid **3**, leflunomide **4**, cloxacilin **5**, rimonabant **6**, celecoxib **7**, combretastatin A-4 **8**, and benzo[f]chromen-indole **9** (Fig. 1) [12–14]. US technology offers mild reaction

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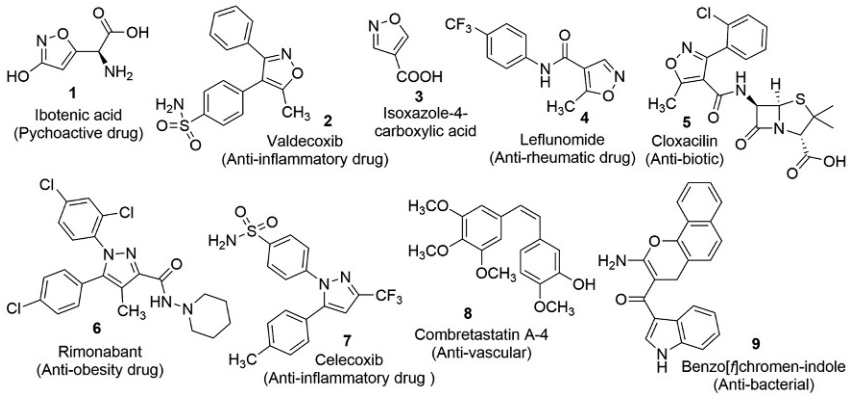


Fig. 1 Selected examples of biologically active.

conditions, reduces energy consumption, permits the use of cheaper and lower purity reagents, uses less hazardous chemicals, increases product selectivity, reduces the number of synthesis steps, eliminates the necessity of the use of additional costly solvents, enhances and promotes the reaction rate and can influence the activity of a catalyst [15]. All these facilities make the application of US very striking for polymer degradation and synthesis [16, 17], metallic compounds synthesis, green organic synthesis, synthesis of nanomaterials in environmental remediation (AOPs), and many other applications, although a large-scale operation still remains out of reach [18–20].

1.3 Origin of the sonochemical effect

Recently, sonochemical irradiation has gained major consideration owing to its ability to facilitate unique physical and chemical conditions. The utility of ultrasound for the preparation of compounds offers an alternate energy source to those used in conventional chemistry, where usually either heat, electromagnetic waves (e.g., light, microwaves), or electricity are used [21–23]. The actual chemical activation mechanism operates during sonication. This phenomenon, however, does not derive from the direct interaction of US rays with substance via coupling to electronic, rotational, or vibrational molecular states, but rather from a secondary phenomenon called as acoustic cavitation: the creation, growth, and collapse of a cavitational bubble in the liquid medium [24, 25]. To be more precise, when liquids are irradiated with US in the frequency spectrum from 20 kHz to 500 MHz, the high tensile stress during rarefaction cycles can cause local rupturing of the liquid at weak spots [15]. These weak spots may include preexisting pockets of gas (e.g., *air*/nitrogen), solid impurities, or dust particles in the fluid. During one or several cycles, the formed cavities grow into microbubbles until reaching a maximum size of $\sim$100–150 μm before experiencing implosive collapse. Upon the collapse of a bubble, some infrequent reaction conditions will be produced: high velocity microjets, high pressure of around 1000 atmosphere, high temperature of about 5000 K and powerful shock waves. It is this library of events encompassing the inception, expansion, and implosion of

microbubbles that is named acoustic cavitation and the area related with its application to the synthesis and modification of matters is called as sonochemistry [15, 26]. The sonochemical phenomenon is justified to be caused by the development of a so-called thermal "hot spot" during the process of cavitational collapse. Cavitation is the core of the sonochemical phenomenon and hence, serves as an vital bond between US and chemistry or a bridge between the chemical effects and the physical pressure variation of the sound wave [2]. However, apart from the chemical phenomenon, cavitation can also induce physical effects; for example, turbulence, micro-jetting, micro-streaming, etc. Generally, there are numerous factors influencing sonochemical action, these include the characteristics of the liquids used such as surface tension, purity (e.g., dissolved solids), viscosity, and solvent and solute vapor pressure as well as sonication parameters such as amplitude and frequency. Hence, the chief task in sonochemical applications is the choice of the appropriate bubble behavior for the required phenomenon [25].

1.4 Sonochemical device

Fig. 2 demonstrates a typical laboratory-scale sonochemical device. A high-intensity US titanium (Ti) horn is joined to a transducer. The transducer transform electrical power coming from a generator to mechanical energy in the form of US vibration. USI tool also contains an US bath with gas inlet/outlet branches. For controlling the temperature of the US bath, generally double walled vessels are employed [27].

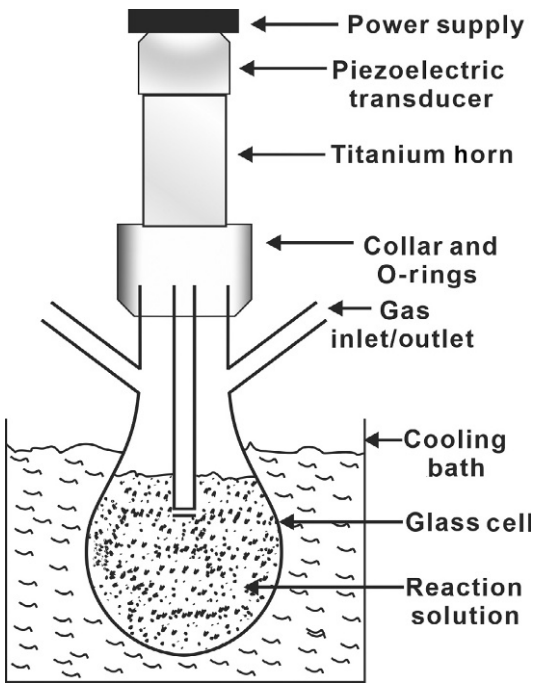


Fig. 2 A laboratory-scale high-intensity ultrasound apparatus.

1.5 Ultrasound-assisted solvent-free organic synthesis

Solvent-free organic synthesis (solvent-less organic synthesis) has received considerable attention attributed to the rising concern for the impact of solvents on human body and on the environment, apart from simplicity in the processes and economic demands [28, 29]. Thus, from an ecological point of view, without a doubt, the best solvent is no solvent. There are obviously numerous great reactions that can already be performed under solvent-less conditions. Examples that spring to mind are many polymerizations and the several industrially significant gas-phase reactions. Pericyclic reactions, in particular the Diels-Alder (D-A) reactions, are also frequently performed in the absence of solvent [28]. However, over the past few years, research documents on solvent-free reactions have been gradually frequent and this field has become a hot topic of research. On another note, as described in Section 1.2, employment of US energy in chemical conversion is an effective and attractive method. Therefore, US irradiation coupled with solvent-free conditions results in formation of green synthetic system together with considerable improved selectivity, cleaner reactions, milder reaction conditions, higher yields and reduction of reaction times, thus offering a great tool in circle of synthetic chemistry. In the past years, tremendous outcomes have been noticed from the US prompted solvent-free organic synthesis in terms of energy, yield, time, cost, and selectivity [4–6, 11, 13, 17, 20, 23].

1.6 Aim and scope of this review

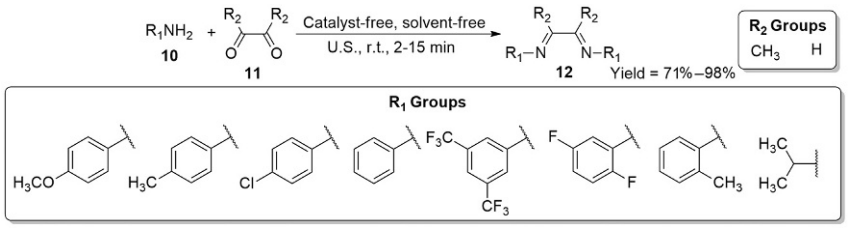
In this chapter, a critical review and analysis of the literature on ultrasound-assisted solvent-free synthesis has been presented by focusing on the applications of US rays in polymerization reactions, coupling reaction, protection/deprotection reactions, addition reactions, reduction, oxidation, substitution reactions, condensation reactions, and heterocyclic chemistry, etc. The chapter has been divided into two main sections based on either the ultrasound-assisted solvent-free synthesis is under catalytic conditions or catalytic-free conditions. Cons and pros of each reaction are discussed in detail. The goal of this chapter is to increase the use of ultrasound-assisted solvent-free approach for production of organic products in economic competitive and sustainable manner with the least impact on the environment. It is expected that this chapter is highly helpful to identify and analyze critical issues, barriers, and opportunities, which will be beneficial in conducting future research and for new ideas in the quest for rational designs of more promising ultrasound-assisted solvent-free synthetic approaches.

2. Ultrasound-promoted catalyst-free organic synthesis under solvent-free conditions

2.1 Synthesis of *N,N′*-dialkyl- and *N,N′*-diaryl-1,4-diazabutadienes

1,4-Diazabutadiene analogous **12** are of great significance in fine chemical owing to their employments as mesoporous material and liquid-crystalline polymers, mainly as

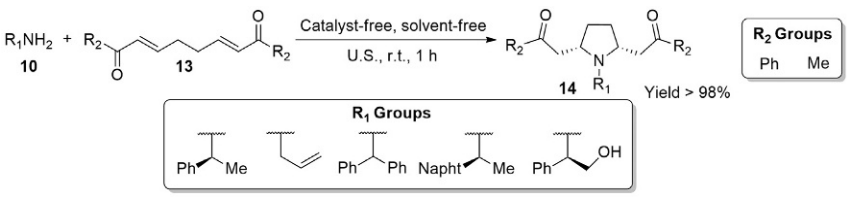
intermediates for formation of several transition metal composite, which have been utilized as catalytic systems in olefin epoxidation, olefin polymerization, and other valuable approaches [30, 31]. An ultrasound-assisted novel, efficient, versatile, convenient, and ecologically safe technique for synthesis of *N*,*N*′-dialkyl- and *N*,*N*′-diaryl-1,4-diazabutadienes **12** in good to excellent yield (71%–98%) through smooth condensation of amines **10** with α-diketones **11** in the absence of solvent was described by H. Yan and coworkers (Scheme 1) [32]. Apart from simplicity in experiment, the chief benefits of the methodology are high yields (71%–98%), short reaction time (2–15 min), mild conditions, and reduce toxicity.



Scheme 1 Formation of 1,4-diazabutadienes under sonication conditions.

2.2 Diastereoselective sequential one-pot double aza-Michael preparation of pyrrolidines

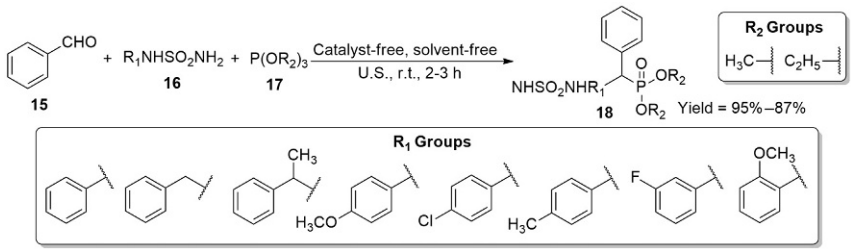
2,5-Difunctionalized pyrrolidines **14** are naturally ubiquitous, biologically important substances and the preparation of this type of alkaloids is of considerable current attention [33, 34]. Joseph and coworkers described an effective, green procedure for the ultrasonication-assisted formation of *meso*-2,5-difunctionalized pyrrolidines **14** in excellent yield (>98%) from commercially available symmetrical double Michael acceptors by means of a double aza-Michael (DAM) approach (Scheme 2) [35]. The main step depended on an aza-Michael addition of primary alkylamine derivatives **10** to symmetrical (*bis*)-α,β-unsaturated substrates **13**. US activation united with solvent-less conditions result in the formation of corresponding pyrrolidine derivatives **14** in excellent stereoselectivities and quantitative yields within short reaction times (1 h). The optimized reaction conditions have been extended to the ultrasonic-assisted predation of pyrrolidine *Lobelia* alkaloid derivatives in short sequences.



Scheme 2 Ultrasonication-assisted formation of pyrrolidine derivatives.

2.3 Three-component one-pot prepartion of α-sulfamidophosphonate derivatives

α-Sulfamidophosphonate derivatives **18** have found a broad spectrum applications in the field of biological chemistry. They are found to be potent antibiotics, pharmacological agents, peptidomimetics, and enzyme inhibitors [36–38]. Berredjem and coworkers reported an effective and facile three-component one-pot prepartion of *α*-sulfamidophosphonate derivatives **18** in high yields (95%–87%) via condensation reaction of sulfonamide **16**, aryl aldehyde **15,** and *tri*-alkyl phosphite **17** under US irradiation (40 kHz) without catalyst and solvent at ambient temperature (Scheme 3). This synthetic approach delivers a unique tool for the formation of significant bioactive *α*-sulfamidophosphonate analogues **18** [39]. This system was recognized with various benefits, including the environmental friendliness, mild reaction conditions, simple work-up procedures, excellent yields, and short condensation times (2–3 h).



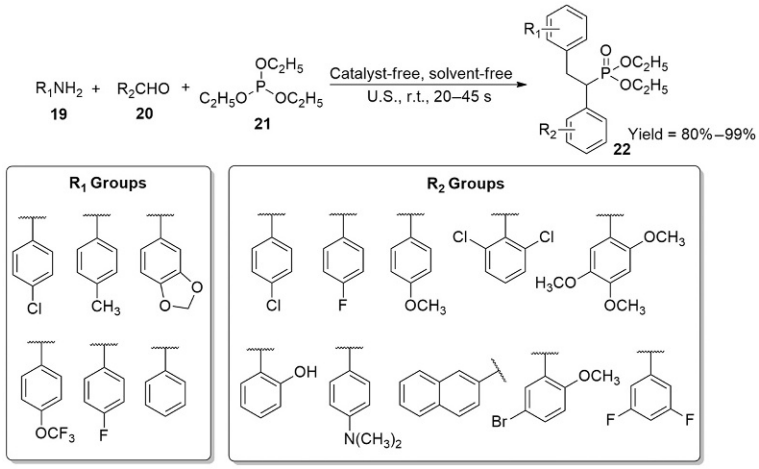
Scheme 3 Condensation reaction of unique *α*-sulfamidophosphonates.

2.4 One-pot creation of *α*-aminophosphonate frameworks

α-Aminophosphonates **22** are amongst the most investigated biologically active substances which are documented to contain antitumor, antibiotic, and anti-inflammatory potencies. Their potential is also well reported as good insecticides plant growth regulators, fungicides, peptide mimetics, herbicides, enzyme inhibitors, etc. [40, 41]. An US-assisted environment friendly, efficient and easy process was reported by Dar et al. for the formation of *α*-aminophosphonate derivatives **22** within seconds (30–45 s) via a three-component one-pot reaction of amine derivatives **19**, aldehyde derivatives **20,** and *tri*-ethyl phosphite **21** under mild conditions in excellent yield (80%–99%) (Scheme 4). Under catalyst-free and solvent-less conditions, the targets **22** were attained in high purity, high selectivity, and high yields [42].

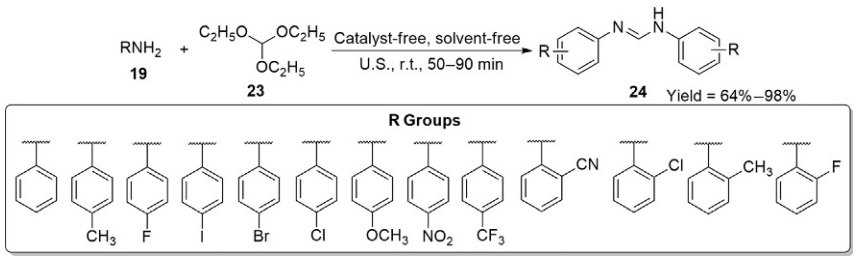
2.5 Preparation of *N,N′*-diarylfunctionalized formamidines

Heterocycles bearing formamidine skeleton **24** have been investigated widely on account of their important applications as protecting groups for primary amines, bleaching agents



Scheme 4 Condensation of anilines, benzaldehydes, and triethylphosphosphite.

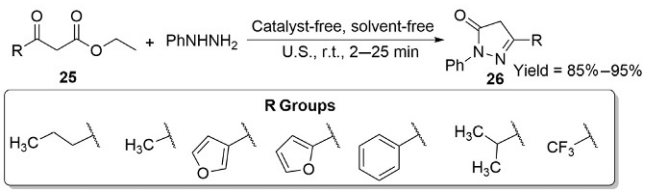
for paper, ultraviolet light absorbers, building blocks in polymer synthesis, chelating or bridging modes, synthons for various chemical transformations and bioactive molecules [43, 44]. B. A. Dar and coworkers described an effective and mild technique for the formation of *N*,*N*′-diarylfunctionalized formamidines **24** in 64%–78% yield via reaction of electronically and structurally divergent amines **19** with *tri*-ethoxymethane **23** under environment-friendly conditions for 50–90 min (Scheme 5). Ultrasonic power was used to deliver the required compounds **24** in high purity with high yields under catalyst-free and solvent-less conditions [45]. Targets compounds **24** were purified via crystallization method to prevent excess use of organic solvents. The easy purification, simple workup and rapid kinetics under milder conditions are key benefits of this procedure. As compared to conventional approaches, in which potentially dangerous additives or/and catalysts were used [43], this technique is acid/metal catalytic system with no side reaction, circumvents the employment of any base, requires short reaction times, easy to handle, inexpensive and delivers simple purification of products through nonaqueous workup.



Scheme 5 Formation of *N*,*N*′-diarylfunctionalized formamidines at ambient temperature.

2.6 Synthesis of substituted pyrazolone derivatives

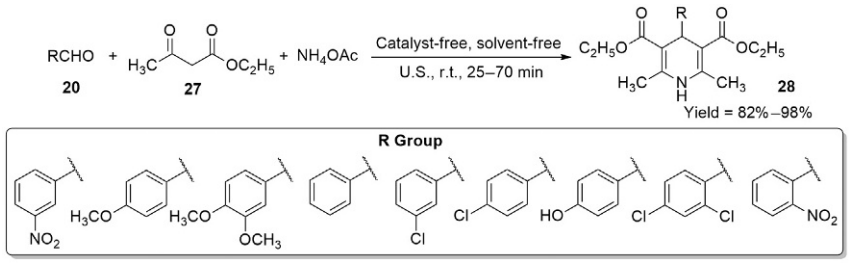
Pyrazolones **26** are of huge significance in medical chemistry on account of their various applications as antiphlogistic, uricosuric, anti-arthritic, antipyretic, and analgesic characteristics. Also, these compounds **26** are suitable intermediates for industrial synthesis of color photographical compounds, thermally stable polymers, dyes, liquid crystals and herbicides [45, 46]. Mojtahedi and coworkers disclosed an effective and rapid solvent-less technique for the synthesis of functionalized pyrazolones **26** via smooth condensation reaction of various β-keto esters **25** with phenylhydrazine under ultrasonic conditions at r.t. within 2–25 min (Scheme 6). Yields of synthesized pyrazolones **26** are excellent (85%–95%), no extra catalysts or additives are required, and reactions proceed at ambient temperature [47].



Scheme 6 Preparation of substituted pyrazolone derivatives.

2.7 Development of 1,4-dihydropyridine scaffolds

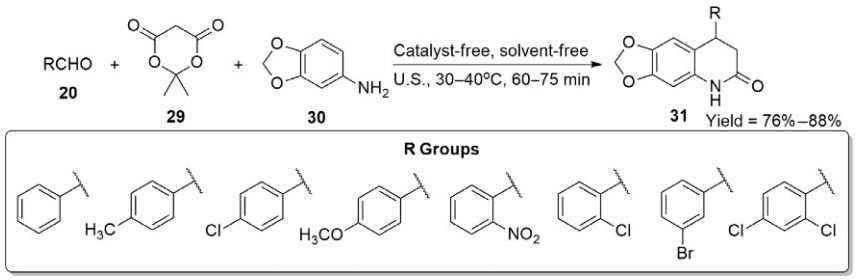
1,4-Dihydropyridine derivatives **28** (1,4-DHPs) have gained much consideration because of their broad range of medicinal and pharmacological affinities; for instance, antitumor, antihypertensive, and antibacterial effects [48, 49]. Wang and coworkers reported an efficient, convenient and versatile protocol for forming 1,4-dihydropyridine scaffolds **28** (1,4-DHPs) in 82%–99% yields via condensation reaction of aryl aldehydes **20**, ammonium ethanoate and ethyl acetoacetate **27** under sonication conditions in the absence of solvent and catalyst at ambient temperature for 25–70 min (Scheme 7). This procedure optimized the Hantzsch reaction, which has numerous noticeable benefits including solvent-less, catalytic-free, mild conditions, less toxic, simple workup, short reaction times, and excellent yields [50].



Scheme 7 Condensation of ammonium acetate, ethyl acetoacetate, and aldehydes.

2.8 Preparation of 8-aryl-7,8-dihydro-[1,3]-dioxolo[4,5-g]quinolin-6 (5H)-ones

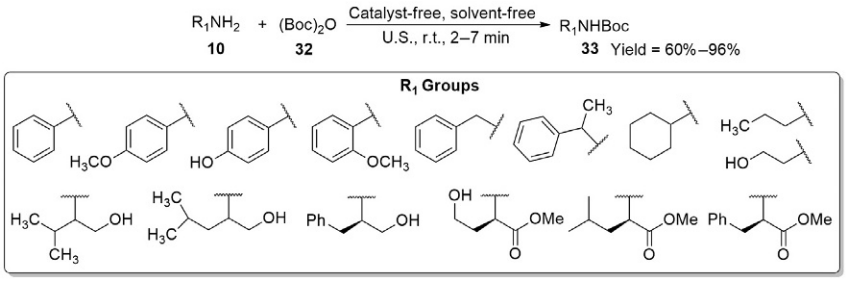
Quinoline derivatives **31** are significant family of biologically active compounds containing numerous pharmacological abilities, particularly antimalarial potency [51, 52]. After observing this, Azarifar and Sheikh reported a straightforward, effective, US-prompted one-pot useful technique for the formation of unique 8-aryl-7,8-dihydro-[1,3]-dioxolo [4,5-g]quinolin-6-(5*H*)-ones **31** through the three-component condensation of several aryl aldehydes **20**, 3,4-methylendioxyaniline **30,** and isopropylidene malonate **29** under solvent-less and catalyst-free conditions at temperature in the range of 30–40°C for 60–75 min (Scheme 8). Good yields of the targets **31** (76%–88%), catalyst- and solvent-free conditions, mild reaction condition, and environmentally friendly procedure are the core merits of this procedure [53].



Scheme 8 Reaction of aryl aldehydes, 3,4-methylendioxyaniline and isopropylidene malonate.

2.9 *t*-Butoxycarbonyl-mediated protection of aromatic and aliphatic amine derivatives

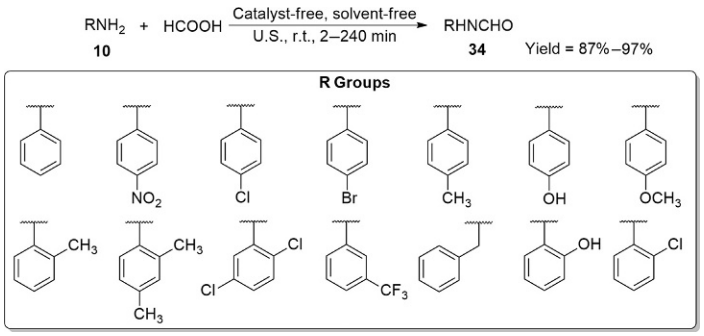
Protecting amine moiety is very vital attributed to their existence in numerous precursors and in diverse range of bioactive compounds [54]. Among various protecting groups, the *tert*-butoxycarbonyl (Boc) moiety has an extensively valuable functionality for protecting amine moiety. Popularly of Boc-based protection is mainly because of the great resistance to nucleophilic and basic conditions, the promising stability of the *N*-Boc moiety toward catalytic hydrogenolysis and its labile nature under numerous chemical conversions [55]. A simple and green method for the *N*-Boc protection on aromatic and aliphatic amine derivatives **10** under sonication conditions was described by Amira and coworkers. To be more precise, environmentally benign, efficient, highly chemoselective *N*-Boc protection of several amines **10** was accomplished, from reaction of amines **10** and di-*t*-butyl dicarbonate $(Boc)_2O$ **32** at room temperature, in good to excellent isolated yield (60%–96%) in a short reaction time (2–7 min) without formation of *O*-*t*-Boc, *N*,*N*-di-*t*-Boc, urea or isocyanate as side products (Scheme 9) [55]. Absence of any auxiliary substances, an easily available and inexpensive reagent, and mild conditions are the core benefits of this method.



Scheme 9 Boc-based protection of amine analogous.

2.10 *N*-Formylation of aromatic amine derivatives

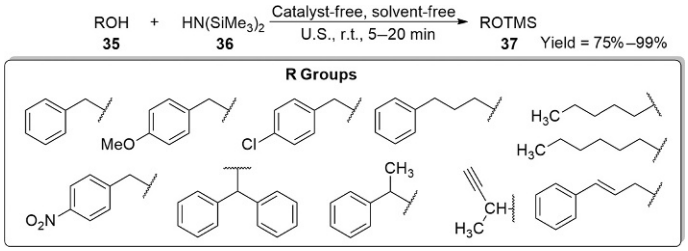
The *N*-formylation of amine moieties **10** is a highly valuable synthetic step in the preparation of useful products in drug discovery [56]. *N*-Formyl entities **34** have been widely used in diverse range of reactions, for instance as a precursor for the preparation of imidoformamides or carbylamines and as an important amine-protecting group in synthesis of peptides, and hydrosilylation of carbonyl compounds or preparation of acyl chlorides from carboxylic acids [57]. Habibi and coworker reported a safe, efficient, fast, and economically and environmentally benign technique for the *N*-formylation of amines **10** via reaction of anilines **10** with HCOOH under catalyst-free and solvent-less conditions under sonication conditions at ambient temperature for 2–240 min in excellent yield (87%–97%) (Scheme 10) [58]. This methodology has the advantages of outstanding reaction rates and yields, higher purity and yields, shorter reaction time, excellent chemoselectivity, cleaner reaction profiles, mild and green reaction conditions, simple methodology, and easy workup, in which the purification procedures are not essential to obtain the pure products **34**. The approach is appropriate to both the large and small scale and can also be utilized for the insertion of other amine protecting moieties.



Scheme 10 Green *N*-formylation of amine moieties.

2.11 Protecting alcohol moieties through formation of silyl ethers

Owing to diverse organic, medicinal, and analytical chemistry uses of protected hydroxyl functionalities (e.g., **37**), they are very significant precursors [59]. Numerous organic reactions as well as multistep syntheses contain at least one step of OH moiety protection. In this context, one of the most frequent approaches is to transform alcohols **35** into their respective silyl ethers **37** [60]. M.M. Mojtahedi and coworkers presented an effective, fast, and chemoselective technique for protection of alcohols **35** in good yields (75%–99%) within short reaction times (5–20 min) by converting them into silyl ethers **37** [61]. To be more precise, numerous kinds of phenols and alcohols **35** were quickly protected using *bis*(trimethylsilyl)amine **36** in high yields at ambient temperature using high-intensity US rays in the absence of any additive and solvent (Scheme 11). The corresponding silyl ether targets **37** are simply achieved from the reaction content by simply evaporating the volatile portion. Also, for protecting sterically less hindered alcohol moieties **35**, appropriate chemoselectivity was noticed.



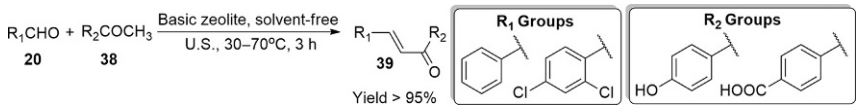
Scheme 11 Protection of alcohols by the formation of silyl ethers.

3. Ultrasound-assisted catalytic organic synthesis under solvent-free conditions

3.1 Amino grafted zeolite-catalyzed synthesis of *trans*-chalcones

The members of the flavonoid and chalcone class have gained a huge deal of attention owing to their employments as anticancer, anti-inflammatory, and antibacterial drugs [62, 63]. Chalcone derivatives **39** are significant precursors in the preparation of numerous pharmaceuticals. The solvent-free, selective synthesis of *trans*-chalcones **39** in excellent yield (>95%) *via* ultrasound-assisted amino-zeolites-catalyzed Claisen-Schmidt reaction of acetophenones **38** with benzaldehydes **20** at 303, 323, and 343 K for 3 h was developed by Martin-Aranda and coworkers (Scheme 12) [64]. The basic NH_2-zeolites (CsNaX-NH_2 and NaX-NH_2) were formed by grafting 3-(trimethoxysilyl)propylamine onto CsNaX and NaX and zeolites, respectively. The observed order of activity was NaX-NH_2 < CsNaX-NH_2. In this solvent-free, green technique, when cesium exchanged X-NH_2 is utilized under US activation, chalcone derivatives **39** are selectively formed in excellent yields (>95%). Of note, no side-products were noticed, which indicate that

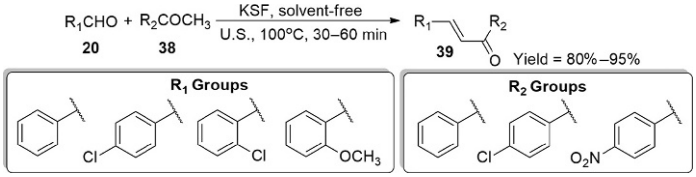
Cannizaro reaction or ketone auto-condensation does not occur under amino grafted zeolite experimental conditions. Thus, this technique provides a state-of-art alternative to classical heating catalysis and the procedure itself is eco-friendly with negligible waste.



Scheme 12 Amino-zeolites-catalyzed Claisen-Schmidt reaction of benzaldehydes and acetophenones.

3.2 Acid-clay-catalyzed synthesis of synthesis of *trans*-chalcones

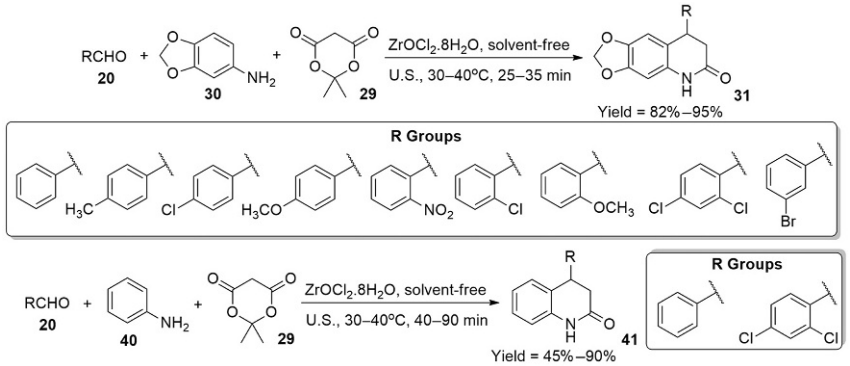
Trabelsi and coworkers presented an advanced formation of *trans*-chalcone derivatives **39** in excellent yields (80%–95%) within 30–60 min, from reaction between aryl aldehydes **20** and aryl methyl ketones **38**, catalyzed by commercially available acid-clay (namely, montmorillonite KSF) under sonication conditions (Scheme 13). Furthermore, the *trans*-chalcone derivatives **39** were formed at moderate temperatures reaction (100°C) and in high selectivity using a reduced proportion of the acid clay-catalyst. This approach was environmentally friendly and rapid as the formation was performed under solvent-free conditions [65].



Scheme 13 Acid-clay-catalyzed Claisen-Schmidt reaction between benzaldehydes and aromatic methyl ketones.

3.3 Zirconyl chloride-catalyzed preparation of 3,4-dihydro-2(1*H*)-quinolinones

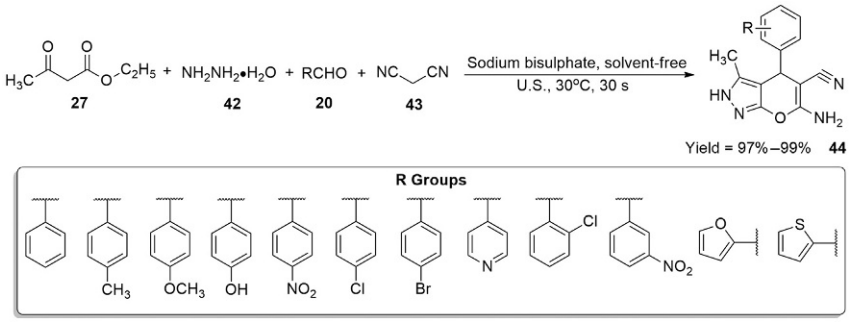
Quinoline derivatives (**31** and **41**) are a well-known class of heterocyclic compounds not only in medicinal science, on account of their extensive occurrence in drugs and natural products, but also in optoelectronics, electronics, and polymer chemistry for their tremendous mechanical characteristics [52, 66]. A solvent-free, three-component, convenient reaction of aromatic aldehydes **20**, Meldrum's acid **29**, and amines (**30** and **40**) to deliver 4-aryl-3,4-dihydroquinolin-2-(1*H*)-ones **41** and 8-aryl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6-(5*H*)-ones **31** in the presence of zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$-a nontoxic and efficient catalyst) under ultrasonic irradiation conditions at 30–40°C for 25–35 min was described by Azarifar and Sheikh (Scheme 14) [67]. This novel procedure provides numerous benefits, including solvent-free conditions, good yields (82%–95%), use of recyclable and green catalytic system, easy workup, clean reaction, and low catalyst loading.



Scheme 14 Zirconyl chloride-catalyzed reaction of Meldrum's acid, aryl aldehydes, and amines.

3.4 Sodium *bi*sulfite-catalyzed preparation of pyrano[2,3-c]pyrazole derivatives

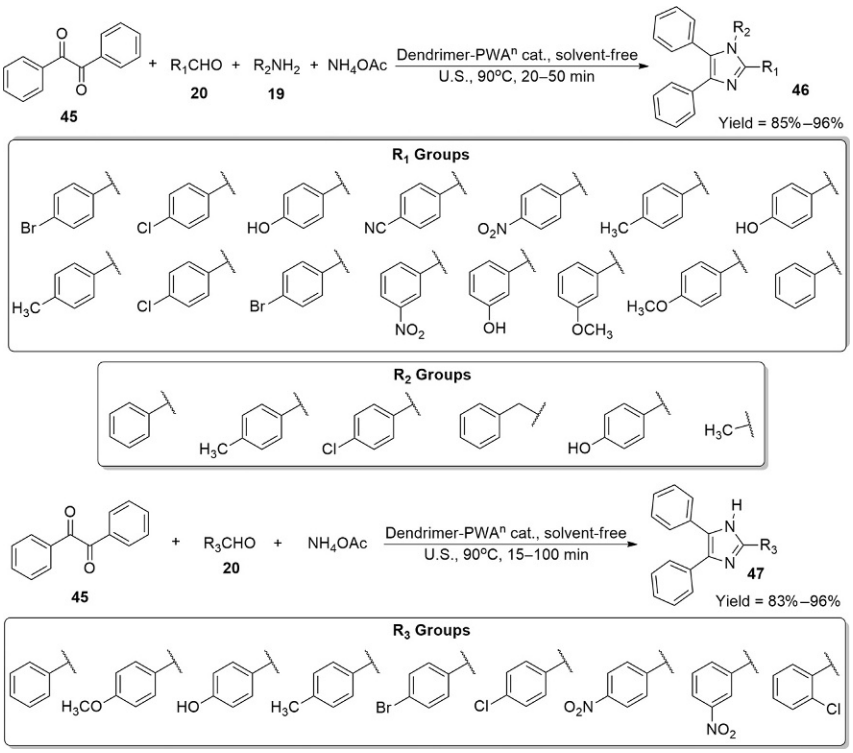
Pyrano[2,3-c]pyrazole derivatives **44** is a developing family of heterocyclic compounds and is extensively explored as it is a significant structural centerpiece of the developing drugs together with broad range of pharmaceutical applications as potential anti-inflammatory, anticancer, analgesic, molluscicidal activity, inhibitors of human Chk1 kinase, and as antimicrobial [68]. B. Shined and coworkers described a highly practical, convenient, economically lucrative, and efficient environment friendly approach for US promoted formation of 6-amino-4-phenyl-3-methyl-2,4-dihydropyrano[2,3-c] pyrazole-5-carbonitriles **44** (substituted pyrano [2,3-c]pyrazoles) within very short reaction time (30 s) in high yields (97%–99%) via multicomponent reaction of various aldehydes **20**, acetoacetic ester **27**, hydrazine hydrate **42**, propanedinitrile **43** in the existence of sodium *bi*sulfite as a catalyst (Scheme 15) [69]. The main properties of this procedure are excellent yields and shorter reaction time, building the procedure economically lucrative and environment friendly. Also, the technique is practical, robust, and simple, which required routine reagents and proceeds without any special handling method.



Scheme 15 Sodium bisulfite-catalyzed synthesis of pyrano[2,3-c]pyrazole derivatives.

3.5 Dendrimer-PWA^n nanoparticles-catalyzed synthesis of multi-substituted imidazoles

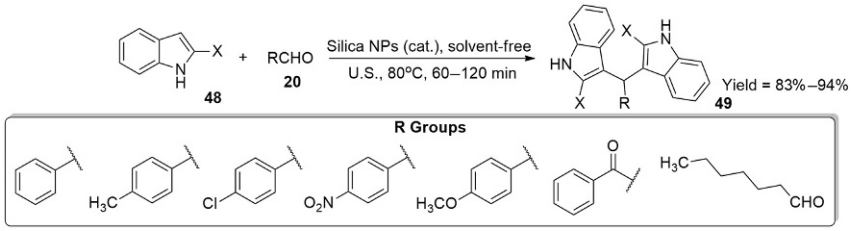
Imidazole moiety (e.g., **46** and **47)** is the structural centerpiece of numerous significant drugs; for example, Trifenagrel, Eprosartan, Olmesartan, and Losartan [70]. Multifunctionalized imidazole moieties (**46** and **47**) have been the current mediators in several heterocycles of potent bioactivity and have attained the consideration of chemists for over a century [71]. M. Esmaeilpour and coworkers reported nano-silica dendritic polymer-matrix $H_3PW_{12}O_{40}$ nanoparticles (dendrimer-PWA^n) as a reusable catalytic system for the preparation of biologically active three 2,4,5-*tri*functionalized and 1,2,4,5-*tetra* functionalized imidazoles (**46** and **47**) in high yields (83%–96%) within 20–50 min via condensation of primary amines **19**, aldehydes **20,** and ammonium acetate and benzil **45** under ultrasonic irradiation and solvent-free conditions (Scheme 16) [72]. The catalytic system is easily isolated from the synthesized imidazoles by filtration and also shows outstanding recyclable potency. The key points for this environmentally friendly and efficient method are simplicity, easy recovery, and reuse of the catalytic system, high yields, short reaction times, easy work-up technique, generality and efficiency, making it an attractive and useful method for the formation of highly functionalized imidazoles (**46** and **47**).



Scheme 16 Dendrimer-PWA^n nanoparticles-catalyzed formation of *tetra*-functionalized and *tri*-functionalized imidazoles.

3.6 Nano SiO_2-catalyzed synthesis of 3,3-(methylene)*bis*(coumarins)

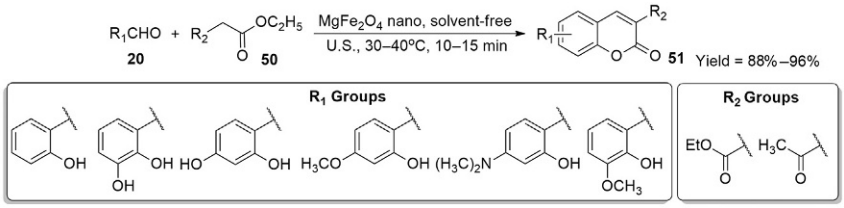
3,3-(Methylene)*bis*(coumarins) **49** (*aka*. *bis*(indolyl)methanes or *bis*coumarins-the bridge substituted dimers of coumarin) are significant family of heterocycles and used as antiseptics, urease inhibitors, antifungals, antipyretics, and anti-inflammatories [73]. An efficient and green procedure for the formation of 3,3-(methylene)*bis*(coumarins) **49** via condensation reaction between carbonyl entities **20** and indoles **48** in the presence of nano-silica gel as a catalyst under sonication conditions in high yields (83%–94%) with short reaction times (60–120 min) was disclosed by Ghodrati and coworkers (Scheme 17) [74]. Native nano-silica gel (nano SiO_2) was utilized as a readily available and inexpensive catalytic system in the absence of any support of matrix or surface variation on it. Excellent yields, tremendous chemoselectivity, environmentally friendly conditions, quick and easy isolation of the products and short reaction time are the key merits of this methodology. Recovery and reusing of the nano-SiO_2 catalytic system were also investigated, revealing that the catalytic system is easily isolated by filtration from the products **49** and also displays amazing recyclable activity.



Scheme 17 Nano SiO_2-catalyzed condensation of indoles with carbonyl compounds.

3.7 $MgFe_2O_4$ nano-catalyzed synthesis of coumarins

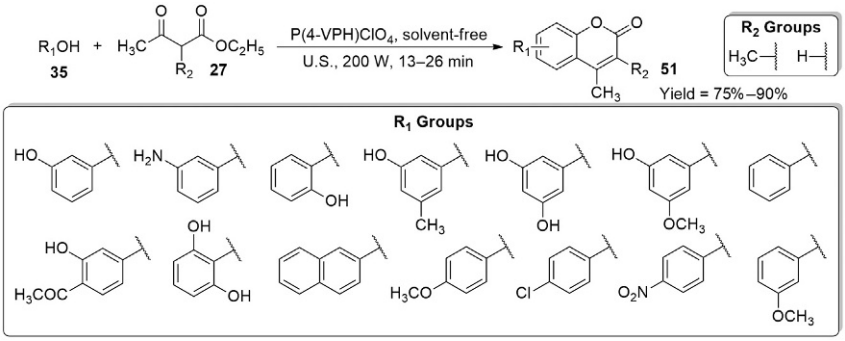
Coumarin derivatives **51** are significant family of heterocyclic compounds. Coumarin derivatives **51** have gained growing consideration attributed to their broad spectrum of applications; for instance, anticoagulant, antibacterial, anti-hepatitis C virus, antitumor, and spasmolytic properties. Moreover, coumarin derivatives **51** are structural components of several natural products and create pharmacologically active compounds [75, 76]. Ghomi and Akbarzadeh performed the preparation of 3-functionalized coumarin derivatives **51** via the Knoevenagel condensation of benzaldehydes **20** with 1,3-dicarbonyl substrates **50** by using magnesium ferrite ($MgFe_2O_4$) nanoparticles as a magnetically recoverable and highly effective catalytic system under solvent-less conditions using USI (Scheme 18) [77]. The nano-catalytic system was simply recovered by using a bar magnet and recycled for numerous times without important loss of its catalyzing ability. Furthermore, this useful procedure have benefits; for example, short reaction time (10–15 min), light catalyst loading, environmentally benign, solvent-free condition, high yields of coumarins **51** (88%–96%), and simple workup.



Scheme 18 $MgFe_2O_4$ nano-catalyzed reaction of 1,3-dicarbonyl entities with salicylaldehydes.

3.8 Poly(4-vinylpyridinium) perchlorate-catalyzed synthesis of coumarins

The coupling of solid phase catalytic system P(4-VPH)ClO_4 (poly(4-vinylpyridinium) perchlorate) as an activator with ultrasonic conditions in Pechmann condensation without any solvent was developed by Khaligh and Shirini [78]. This developed system was observed to be an eco-benign, recyclable catalytic system for formation of functionalized coumarins **51** via Pechmann condensation of β-keto esters **27** and phenols **35** under sonication conditions (nominal power 200 W and frequency of 35 kHz) at r.t. in high yields (75%–90%) with short condensation times (12–26 min) (Scheme 19). The procedure has numerous benefits; for example, no side reactions, simple experimental procedure, and use of inexpensive catalyst with lower loading. Furthermore, the catalytic system can be recovered and recycled for numerous times without important loss of potency.

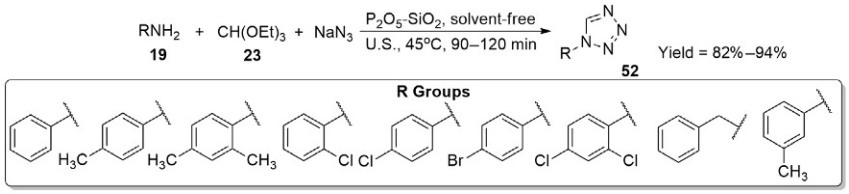


Scheme 19 Solid phase-catalyzed Pechmann reaction of β-keto esters and phenols.

3.9 P_2O_5-SiO_2-catalyzed formation of 1-substituted 1*H*-1,2,3,4-tetrazoles

1-Functionalized 1*H*-1,2,3,4-tetrazoles **52** have been extensively utilized as rocket propellants, as fungicides and herbicides in agriculture and as ligands in coordination chemistry [79, 80]. Nasrollahzadeh and coworkers described a highly effective and simple protocol for synthesis of 1-functionalized 1*H*-1,2,3,4-tetrazoles **52** from the reaction of aromatic amines **19**, 1,1,1-triethoxymethane **23**, and NaN_3 in the presence of P_2O_5-SiO_2 (silica-supported phosphorus pentoxide) as a heterogeneous catalytic system

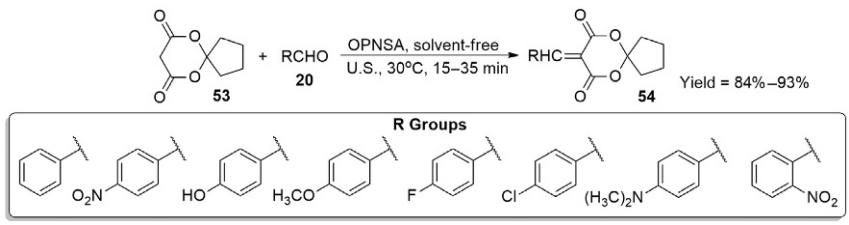
under sonication conditions (90–120 min) in excellent yield (82%–94%) (Scheme 20) [81]. The main merits of this procedure are easy work-up process, low cost, elimination of harmful and dangerous hydrazoic acid, relatively short reaction times and excellent yields. The catalytic system can be recovered through simple filtration and recycled without any significant loss of efficacy.



Scheme 20 P_2O_5-SiO_2-catalyzed reaction of 1,1,1-triethoxymethane, aryl amines, and sodium azide.

3.10 *o*-Phthalimide-*N*-sulfonic acid-catalyzed formation of alkenyl-2,2-butylidene-1,3-dioxane-4,6-dione derivatives

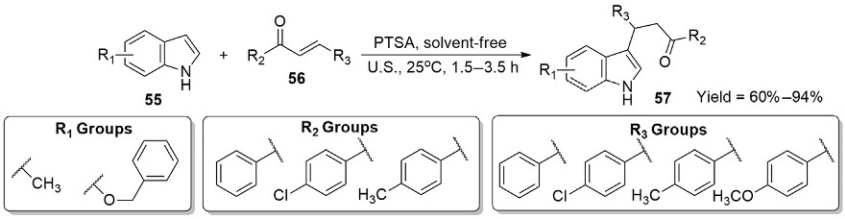
In last two decade, the synthesis of 5-alkenyl-1,3-dioxane-4,6-dione analogous **54** has gained strong attention due to the wide range of their characteristics: these molecules can be utilized as organic compounds with potent bioactivity and useful precursors for a library of natural compounds [82, 83]. Additionally, it also easily reacts with conjugated dienes in D-A cycloaddition or with Grignard reagent in conjugate addition [84]. W. Liao and coworkers synthesized 5-alkenyl-2,2-butylidene-1,3-dioxane-4,6-dione analogous **54** via Knoevenagel condensation of benzaldehydes **20** with 2,2-tetramethylene-4,6-dioxo-1,3-dioxane **53** in the presence of catalytic amount of *o*-phthalimide-*N*-sulfonic acid (OPNSA) under ultrasonic irradiation (15–35 min) without solvent in excellent yield (84%–93%) (Scheme 21) [84]. This protocol has some remarkable benefits such as high yields, less catalyst dosages, and mild reaction conditions with the green aspects by eliminating toxic solvents and catalysts. Also, the catalytic system could be recycled after an easy workup, and utilized at least six times without important decrease in its catalytic performance.



Scheme 21 *o*-Phthalimide-*N*-sulfonic acid-catalyzed reaction of 2,2-butylidene-1,3-dioxane-4,6-dione with benzaldehydes.

3.11 *p*-Toluenesulfonic acid (PTSA)-catalyzed preparation of *β*-indolylketones

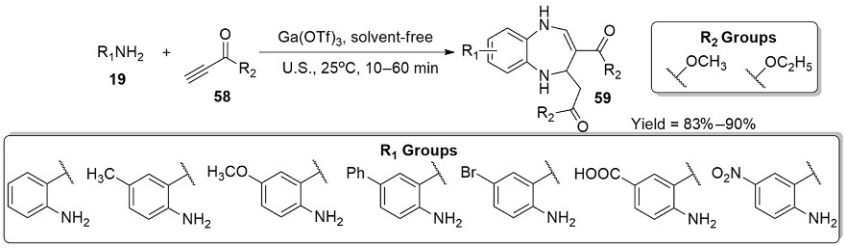
β-Indolylketone derivatives **57** have gained much consideration as significant building blocks for the formation of numerous bioactive entities and natural products [85]. Ji and Wang described the significant catalytic potency of *p*-toluenesulfonic acid (PTSA) as an inexpensive catalytic system, convenient and efficient in US-assisted Michael addition reaction of indoles **55** with *α*,*β*-unsaturated carbonyl ketones **56** at room temperature without solvent (Scheme 22), providing one of the most effective pathway to the formation of *β*-indolylketone analogous **57** in excellent yields (up to 94%) for 1.5–3.5 h [86].



Scheme 22 PTSA-catalyzed reaction of *α*,*β*-unsaturated carbonyl ketones with indoles.

3.12 Gallium(III) triflate-catalyzed [4+2+1] formation of 3,4-difunctionalized-1,5-benzodiazepines

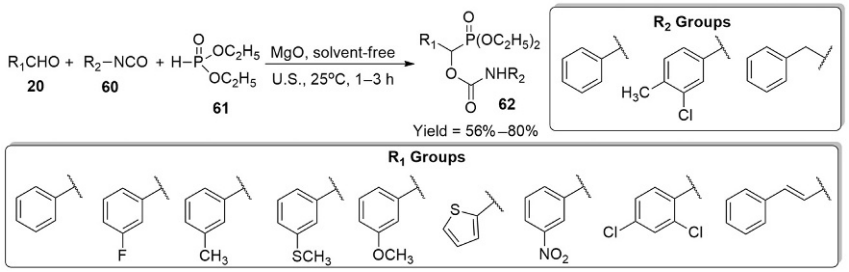
Benzodiazepine derivatives **59** have a broad spectrum of organic and pharmacological properties [87]. Several of these derivatives have been employed as anticonvulsant, analgesic, antianxiety, antidepressive, and anti-inflammatory agents [88]. W. Zhang and coworkers reported a unique [4+2+1] cycloaddition to form a new family of 3,4-difunctionalized 1,5-benzodiazepine derivatives **59** in 82%–90% yields (Scheme 23) [89]. To be more precise, the union of 1,2-phenylenediamines **19** and alkyl propiolates **58** in the presence of $Ga(OTf)_3$ (gallium(III) triflate) under sonication conditions for 10–60 min at 25°C without any solvent afforded 3,4-difunctionalized 1,5-benzodiazepines **59**. Products have a C—C bond, two NH groups and two carbonyl groups, which can be further substituted to make complex heterocycle.



Scheme 23 Gallium(III) triflate-catalyzed reactions of alkyl propiolates with *o*-phenylenediamines.

3.13 Magnesium oxide-catalyzed synthesis of α-oxycarbanilinophosphonates

α-Substituted phosphonic acids are significant precursors for the synthesis of pharmaceutical products and synthetic intermediates [90]. In particular, in the past few years, the synthesis of α-oxycarbanilinophosphonates **62** has gained important consideration attributed to their potential bioactivities and wide employments as dinucleotide analogues or as enzyme inhibitors having antiviral activities. Kaboudin and Fallahi disclosed a green technique for the formation of α-oxycarbanilinophosphonate frameworks **62** via reaction between aryl aldehydes **20** and diethylphosphite **61** in the presence of MgO and subsequent reaction with isocyanates **60** under solvent-less conditions using sonication conditions for 1–3 h in moderate to excellent overall yields (56%–80%) (Scheme 24) [91]. The clean reactions with no tar formation, mild conditions and simple workup are benefits of this technique.



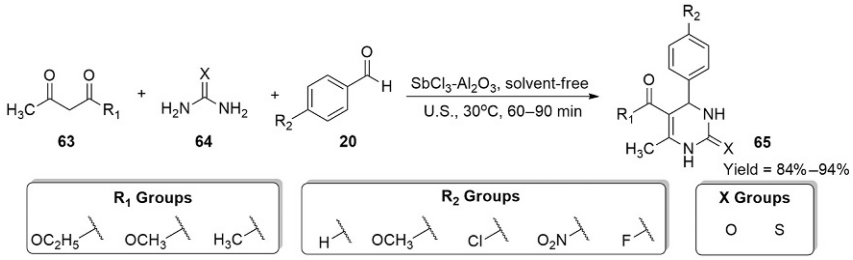
Scheme 24 Magnesium oxide-catalyzed reaction of aldehydes with diethylphosphite.

3.14 Antimony(III) chloride-catalyzed synthesis of dihydropyrimidinones

The dihydropyrimidinones **65** (DHPMs) have gained great attention in the area of medicinal and organic chemistry on account of their attractive array of therapeutic and pharmacological characteristics [92, 93]. Kapoor and coworkers documented solvent-less preparation of dihydropyrimidinone (DHPM) **65** derivatives, in which the antimony(III) chloride ($SbCl_3$; as a Lewis acid) impregnated on aluminum oxide (Al_2O_3) powerfully catalyzes a three-component, one-pot condensation reaction among an aldehydes **20**, a β-ketoesters **63**, and thiourea or urea **64** under ultrasound irradiation conditions for 60–90 min to furnish the respective DHPMs **65** in high yields (84%–94%) (Scheme 25) [94]. The present catalytic system works efficiently in ultrasonic conditions, easy to handle, easily available, and cheap.

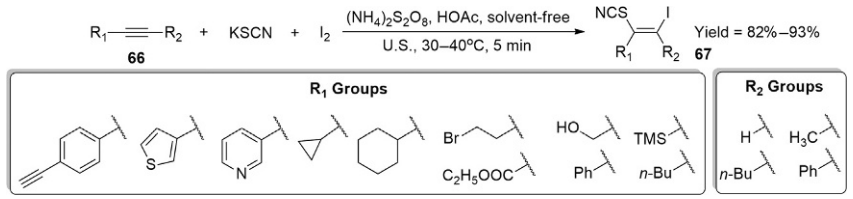
3.15 Potassium thiocyanate/iodine-catalyzed formation of (*Z*)-β-iodo vinylthiocyanate derivatives

(*Z*)-Iodo vinylthiocyanate derivatives **67** represent one specifically remarkable multifunctional compound because both the vinylthiocyanate and vinyl iodo entity are



Scheme 25 Antimony(III) chloride-catalyzed reaction of benzaldehydes, β-ketoester, and thiourea or urea.

valuable in the area of organic transformations and pharmaceutical chemistry [95, 96]. A practical and eco-friendly technique for the multicomponent ultrasound-assisted formation of various (*Z*)-β-iodo vinylthiocyanate derivatives **67** from commercial and cheap alkyne analogues **66**, KSCN and molecular iodine through an intermolecular hydrogen bonding assistance approach was reported by He and coworkers (Scheme 26). This procedure minimizes the harsh reaction conditions, use of large amount of acetic acid, prefunctionalization of alkynes **66** and application of eco-unfriendly transition metal salts. Using USI delivered higher yields (82%–93%) and shorter reaction times (5 min) as compared to classical thermodynamic conditions. The use of a catalytic amount of AcOH significantly improved the stereo- and chemo-selectivity of the iodothiocyanation.

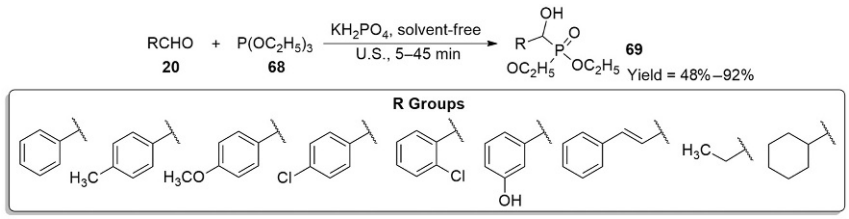


Scheme 26 Reaction of alkynes, molecular iodine, and KSCN.

3.16 Monopotassium phosphate-catalyzed preparation of α-hydroxyphosphonate derivatives

α-Hydroxyphosphonate derivatives **69** are useful precursors for the formation of synthetic intermediates and medicinal compounds. Furthermore, they display antibacterial, anticancer, and antiviral property with the quinoline core [97, 98]. C.H. Gill and coworkers reported a novel, facile, green, and convenient procedure for the preparation of α-hydroxyphosphonate derivatives **69** in fair to excellent yield (83%–94%) from reaction of heteroaromatic/aromatic aldehydes **20** with triethylphosphite **68** in the presence of monopotassium phosphate (KH_2PO_4) under ultrasonication-accelerated solvent-less conditions at r.t. within 5–45 min (Scheme 27) [99]. Application of easy purification,

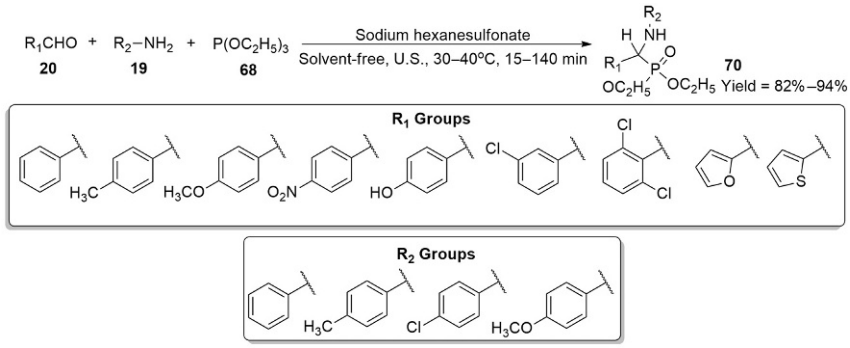
separation, and reaction conditions makes this manipulation very remarkable from an commercial viewpoint.



Scheme 27 Reaction of heteroaromatic/aromatic aldehydes with triethylphosphite.

3.17 Sodium hexanesulfonate-catalyzed formation of α-aminophosphonates

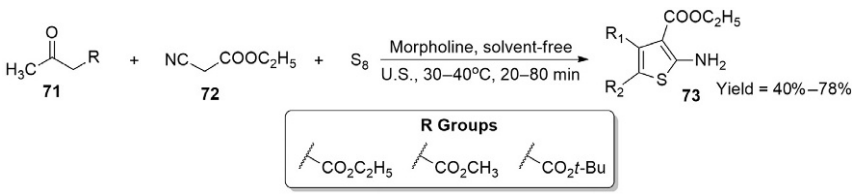
In the past two decades, great concentration has been given on the construction of α-aminophosphonate skeletons **70**, for they are considered to be transition state mimics of peptide hydrolysis and structural derivatives of the respective amino acids. In this context, the services of α-aminophosphonate derivatives **70** as antibiotics, haptens of catalytic antibodies, enzymes inhibitors, peptidemimics, and pharmacologic agents are well reported [100, 101]. Shingare and coworkers described the employment of sodium hexanesulfonate for the preparation of α-aminophosphonate derivatives **70** under USI irradiation in the absence of solvent [102]. To be more precise, sodium hexanesulfonate was observed to be effective and mild catalytic system for the eco-friendly construction of α-aminophosphonate derivatives **70** by the coupling of amines **19**, aldehydes **20**, and triethylphosphite **68** under USI at temperature in the range of 30–40°C for suitable time (15–140 min) to deliver the required targets **70** in high yield (83%–94%) under solventless condition (Scheme 28). This catalytic system offers easy workup, greater selectivity, and clean conversion, making this procedure economically attractive and practical.



Scheme 28 Sodium hexanesulfonate-catalyzed coupling of amines with aldehydes.

3.18 Sulfur/morpholine-catalyzed synthesis of 2-aminothiophenes

2-Aminothiophenes **73** are a significant heterocyclic frameworks of therapeutic and medicinal interest. These moieties **73** exist in numerous relevant heterocycles, various of which show antifungal, antiamoebic, antioxidant, anticoagulant, and antithrombotic potencies [103]. The 2-aminothiophenes **73** are also found in some commercial pills, for example, olanzapine, an antipsychotic medication, used for the treatment of bipolar disorder and schizophrenia. Due to their extensive use, numerous synthetic methods have been reported to produce these heterocyclic compounds **73** [104]. A efficient, fast, and simple solvent-less process for the formation of *tetra*-subtituted 2-aminothiophene derivatives **73** in appropriate yield (40%–78%) from reaction of ethyl cyanoacetate **72** and ketones **71** in the presence of powdered sulfur and morpholine under ultrasonic conditions for 20–80 min was developed by Junior and coworkers (Scheme 29) [105]. The combined benefits of sonochemistry, for instance short reaction times, good yield, and mild reaction conditions, allowed progress to be made in the formation of 2-aminothiophene derivatives **73** through the Gewald reaction.



Scheme 29 Sulfur/morpholine-catalyzed reaction of ethyl cyanoacetate with ketones.

4. Conclusion

Ultrasound, a virtually innocuous and efficient means of activation in synthesis, has been utilized for years with diverse success. The current chapter describes the recent advances on the one-pot multicomponent synthesis of organic compounds using solvent-free techniques coupled with USI. The union of USI with solvent-free techniques in organic synthesis has accomplished some of the objectives of "sustainable and green chemistry" for it has some benefits over the classical thermal approaches in terms of product selectivity, purity, yield, toxicity, and reaction rate, etc. therefore, this powerful tool reduces time, saving money, raw materials, and energy. Anyhow, the key advantages of the use of US-assisted solvent-free synthesis in organic synthesis in comparison to the classical methodologies decrease in the reaction times and an improvement in yields. Also, the US-assisted solvent-free synthetic approach is greener as it uses methodologies in which the volatile and toxic organic solvents are not used. However, the use of US-assisted solvent-free synthesis in synthetic chemistry is still in the initial stage of progress and demands more consideration. Hopefully, this chapter attracts the attention of readers

and creates further interest to consider this precious US-assisted solvent-free method in their future endeavors in planning schemes for the creation of valuable products. Also, the current chapter certainly develops some influences on the ongoing growths in this direction, since it is one of the challenging fields for today's organic methodologists worldwide.

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CHAPTER 6

Sonochemical protocol for biocatalysis

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1. Introduction

1.1 Biocatalysis

Enzymes are made of naturally occurring proteins that can catalyze and regulate several chemical processes inside and outside of the living organisms. They are highly efficient natural biocatalysts that are being extensively favored over chemical catalysts for carrying out numerous industrial processes. They offer distinct advantages, such as high selectivity, specificity, and can be employed at a large-scale level. Moreover, they can carry out reactions at mild experimental conditions where they do not require extreme temperature or pressure unlike chemical catalysts, and therefore are environment-friendly and cost-effective as well. The demand for enzyme-based technologies has been rapidly increasing due to its advantageous properties, cheaper production cost, ability to carry out target-specific reactions, and less or no bioproduct formation at the end of the process. It can be an excellent candidate for industrial development while delivering sustainable processes [1]. Enzymes are being practiced in various distinct applications in the field of textiles, agriculture, food, paper, feed, and leather while achieving a significant reduction in the overall cost of the process. Therefore, most of the industries, including drug, perfumery, textiles, food, leather, cosmetics, and many more have adopted enzyme-assisted processes over conventional methods [2].

1.2 Ultrasonication

Ultrasound, also known as ultrasonic waves, has frequencies higher than the upper audible limit of the human being (>20,000 Hz). Although the adverse effect of ultrasound on several microorganisms and their metabolic activities has been widely studied for decades, the application of US to advance and regulate the activity is very recent. Hence, over the last decade, a massive amount of research has been carried out to attain a deep understanding of the application of ultrasound in several food and biotechnology processes. In earlier research, ultrasound was employed in inactivation of enzymes since it could easily deform the enzyme structure at higher frequencies; however, recent developments in the field

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has proven that the US does not hinder the enzyme activity, particularly, under mild reaction conditions. Moreover, it has been demonstrated that the appropriate dosage of ultrasound frequencies and intensities can drive enhancement in enzyme activity by favoring conformational modifications in protein molecules while maintaining structural integrity. Apart from the level of frequencies and intensities, other operational parameters of ultrasound such as duty cycle of treatment also affect the overall process. Moreover, enzyme-associated factors such as pH, temperature, and enzyme concentration can significantly influence the catalytic activity of enzymes during the ultrasonic treatment. Although enzymes and several other macromolecules that are fragile and are identified to be susceptive to destruction by ultrasound, proper utilization of ultrasound possess a massive potential for amplifying the productivity of several bioprocesses that involves bioactive enzymes in live cells [3, 4]. Therefore, ultrasound can effectively follow the principles of green chemistry and engineering while presenting innovative possibilities for sustainable production of existing and new products and services.

2. Sono-biomechanics of enzymatic reactions

2.1 Biomechanics of enzymes in ultrasound

The enzyme is a protein macromolecule with a large surface area and molecular weight estimated in terms of Daltons (Da). There are hydrophobic and hydrophilic regions on the surface of protein macromolecule [5]. The activation or inactivation of the enzyme is dependent on the parameters used in ultrasound treatment. Due to the effect of ultrasound shock waves, there are several structural changes occur in enzyme structure leading to folding/unfolding. The mechanism insights with respect to sonochemical aspect in enzymatic systems along with changes in the structure of the enzyme have been studied by very few authors [6, 7]. In most of the cases, the reaction is initiated by enzymes and further continued by the cavitation generated by the ultrasound shock waves. During the sonication, it provides both physical and chemical effect by ultrasound including secondary effect, that is, cavitation. The physical effect of ultrasound is basically intense mixing or convection in the medium due to rapid oscillatory motion of fluid elements called microstreaming; whereas chemical effect involves the generation of high temperature and pressure (~5000 K and 1000 atm) resulting in the generation of various oxidizing species such as H°, OH°, 2HO°, H_2O_2, etc. In some cases, the cavitation is intense enough to form phenoxy radicals that also contribute to the reduction reaction of the organic molecules as in case of horseradish peroxidase and laccases, in the presence of phenol molecules. These are highly energetic oxidizing species and able to degrade most of the organic molecules by attacking them instantaneously. This mechanism is applicable in case of enzymes with oxidation or oxidoreductase enzymes like lignin peroxidases, laccases, manganese peroxidases, horseradish peroxidases, etc. [7, 8]. Fig. 1 depicts the graphical representation of the effect of ultrasound on the structure of the enzyme.

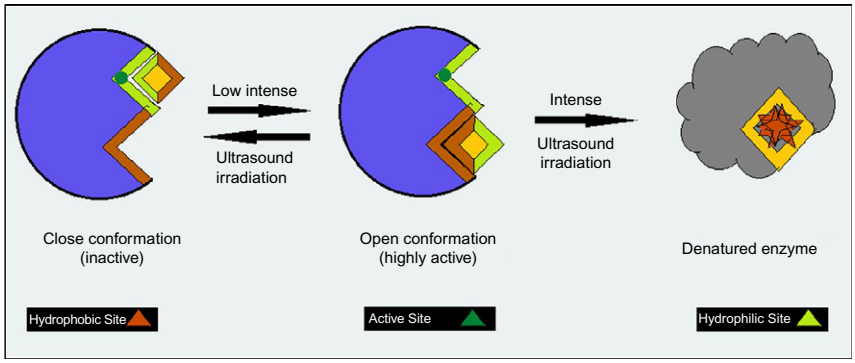

Fig. 1 Graphical representation of the effect of ultrasound on structure of enzyme.

The degradation process employing ultrasound in sonochemical reaction is mainly driven by the radical reaction. The radicals such as OH°, O°, and HO_2° are generated from the transient collapse of the cavitation bubble. These radicals are extremely energetic and react instantly with organic molecules present in the solution. The enzymatic reaction is mainly molecular-based that needs activation energy (E_a) to form *E-S* complex, while the sono-assisted enzymatic reaction has both characteristics; radical reaction and molecular reaction [9]. The sono-assisted enzymatic degradation at static pressure means, at atmospheric pressure, it shows a positive synergistic effect. This is attributed to the cavitation phenomena, which induces both physical and chemical effects in the medium. This results in intense mixing and microturbulence in the medium due to the oscillatory motion of fluid elements as well as the generation of highly oxidizing species that react instantly with organic molecules.

The difference between ultrasound (shock waves of sound) and cavitation effect (generation and collapse of microbubbles) can be understood by studying the biocatalysis at static pressure. Both of these processes produce the physical and chemical effect in the reaction medium. The rise in ambient static pressure of the system alters the characteristic of cavitation bubble by changing the transient and highly energetic motion into stable oscillatory and reduces the generation of radicals as well as the microconvection in the medium [10, 11]. Thus, just by changing the system static pressure, the effects of cavitation could be eliminated completely without altering the effect of ultrasound. For the convenience of the readers, the simulation results of cavitation bubble dynamics model using diffusion-limited model described in few papers [12] that can be applicable for sonochemical biocatalysis.

The mechanism of deactivation of enzymes by ultrasound can be explained as follows. After the US treatment, the unfolded enzyme molecules exposing the catalytic sites cannot refold back due to reduction or reaction of amino acids in the presence of radical. In some cases, there is a generation of radicals (phenoxy) during the degradation of the

substrate which attaches to the reactive sites of the enzyme and blocks them acting as a shield between the enzyme and substrate molecules. These phenoxy radicals can react with each other shielding the active sites can be detrimental if the reaction is not reversible. However, the excess generation of phenoxy radicals leads to a reduction in the interaction between phenoxy radicals and reactive sites of enzyme since they attract other available free radicals toward themselves ending up not interfering with free catalytic active sites of reactions. Also, in the presence of ultrasound, the increase in numbers of collisions between the organic molecules (substrate) and the enzyme enhances the rate of degradation. The intense convection and micromixing in the medium due to ultrasound and cavitation also helps to increase the rate of formation of *E-S* complex as well as rupturing the products from the enzyme that makes the active site available for binding of next substrate molecules to the enzyme [7] and results in enhancement of degradation in the presence of ultrasound. It was also observed that the intermediates formed in advanced oxidation processes combined with peroxidases or laccases (oxidative enzymes) are less toxic compared to the original pollutant. This essentially indicates that the intermediates formed under ultrasound irradiation are lesser toxic than the intermediate formed without ultrasound that confirms the effectiveness of ultrasound on the degradation of organic compounds. It can lead the process toward complete mineralization that can be applied in the field of bioremediation. There are few reviews available exploring the effect of US on enzyme structure in regards to activation and deactivation of enzymatic activity [7]; however, a very few reports were found explaining the structural effects with enzyme-substrate interactions in presence of acoustic cavitation [9].

2.2 Cavitational bubble dynamics

Cavitation is explained as the process of the formation, growth, and subsequent collapse of microbubbles at near adiabatic conditions or cavities lasting only for a minimal time (milliseconds) intervals releasing large amounts of energy into a very small volume of liquid. This phenomenon is represented in Fig. 2. Extremely high energy densities are obtained at localized spots, resulting in high pressures and temperatures. These cavitational effects are observed at multiple locations in the sonochemical reactor. This extreme energy density results in the formation of highly reactive free radicals as well as generation of intense turbulence associated with liquid circulation currents. This phenomenon results in the mechanical or physical effects as well as chemical effects in the liquid medium. These are the several events occurring during acoustic cavitation. The cavitation occurring due to acoustic conditions which are referred to as sound waves (ultrasound). This phenomenon is termed as acoustic cavitation.

Different combination of power and frequency results in different cavitational intensities. As reported in the case of laccases, a high-power low-frequency (22 kHz, 2100 W) and high-frequency low-power ultrasounds (850 kHz, 400 W) were required to achieve

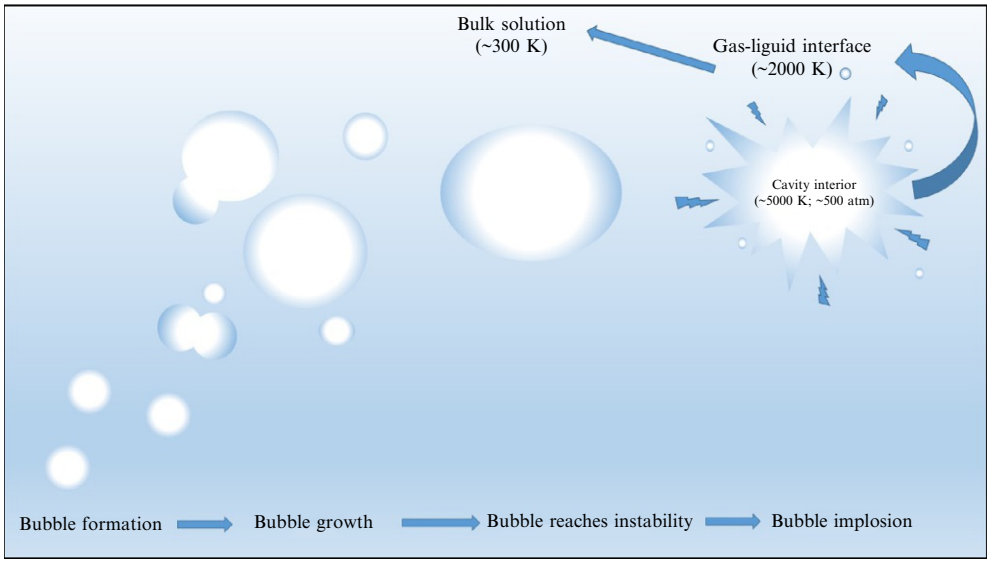

Fig. 2 Graphical representation of cavitation phenomena.

satisfactory results in case of the cotton bleaching process. There are two effects obtained in this case at two different conditions (1) high-frequency ultrasound (850 kHz, 400 W) have assisted laccase pretreatment and (2) high-power ultrasound (22 kHz, 2100 W) have induced bleaching effect due to different cavitational intensities [5]. Combining laccases with the US helped it to reduce the consumption of expensive chemicals, energy, and water. These systems have proved to be promising techniques for reducing the environmental impact and the cost of operations of conventional industrial processes. The use of mediators which acts as electron transporters can further expand the range of laccase substrates to other classes of chemical compounds when used in combination with US [13]. For horseradish peroxidase, the peroxide inactivation by ultrasound follows the first-order kinetics and rate constant increases with respect to the power applied. In the inactivation of peroxidase high-frequency ultrasound such as ultrasound frequency of 378 and 583 kHz (48 W) were particularly effective [9].

Some enzymes like catalase, lysozyme, and alcohol dehydrogenase have been studied with 20-kHz ultrasound bath at varying exposure time and out of these, only catalases had minimum effect on activity, while alcohol dehydrogenase and lysozyme both showed inactivation at an exponential rate. The rate of enzyme inactivation for alcohol dehydrogenase and lysozyme decreased with increasing protein concentration. The inactivation is inhibited by the addition of 2-mercaptoethanol. It was observed that the presence of stainless steel in the sonication vessel has accelerated enzyme inactivation. Thus, based on the observed results, it is suggested that the mechanism of inactivation is chemical rather than mechanical. The comparison is made between the rate of inactivation and

the yield of free radicals by measuring free radical concentration using a radiochemical dosimeter. These conditions are suggested to minimize the sonochemical effects on proteins isolated from cells with an ultrasonic horn [14].

The ultrasound has three major effects such as thermal, cavitation, and mechanical. Due to the combination of these effects, there is an increase in mass transfer in the system, enhancement in the extrusion of media molecules or release of enzyme molecules stored in the cell membrane (in case of cell disruption) and change in media density (owing to size reduction of the substrate in case of lignocellulosic biomass), change in function, and structure of enzyme as well as the substrate. In the case of acoustic cavitation, the collapse of cavitation bubbles produced violent physical forces (e.g., microjets, shear forces, and shock waves) along with the formation of free radicals [11]. Ultrasound is considered as the fundamental process that causes the most chemical reactions in liquids [12]. The acoustic cavitation intensity and ultrasonic frequency are two major factors that affect the production and intensity of liquid cavitation and influence the effect of sonochemical treatment. At the same US frequency, a specific type of enzyme may get deactivated, that is, showing inhibitory effect but at the same time, another enzyme may show enhanced activity in the same mixture. This effect can be used in introducing selective inhibition while selective activation of enzymes. Qu et al. [9] found an increase in the enzymolytic efficiency with the use of continuous single-frequency ultrasound at 33 kHz along with the increase in the inhibitory activity of the angiotensin-converting enzyme (ACE) in wheat germ protein hydrolysates. Ultrasound pretreatment had led to a significant change in the structure of proteins and had improved the functionality of protein hydrolysates [15].

For physical insights into ultrasound-assisted enzymatic reactions, parameters like an analysis of Arrhenius and thermodynamic parameters along with cavitation bubble dynamics are reported. It reveals that the strong microconvection generated by sonication enhances enzyme activity and influence enzymatic reaction kinetics. The cavitation diffusion model has been also reported. The model explains that the US-induced conformational changes in the secondary structure of the enzyme. The fall in frequency factor limits the ultrasound-induced enhancement of biocatalysis. The study has been attempted by Moholkar et al. to obtain physical insight into US-aided enzymatic desulfurization using horseradish peroxidase enzyme for the degradation of dibenzothiophene [12]. The analytical methods like intrinsic fluorescence and circular dichroism spectra of ultrasound-treated enzyme decipher the conformational changes in secondary structure (reduction in α-helix and β-conformations and increase in random coil content) leading to enhancement in the activity. Along with this the radicals generated due to transient cavitation increases the desulfurization kinetics. However, the shock waves result in random motion of enzyme molecules which reduces frequency factor and limits the ultrasonic enhancement of enzymatic desulfurization to a lesser extent [12]. This basic mechanism of sonochemical biocatalysis explained here can be similar to a larger extent for the various chemical reaction catalyzed by enzymes such as oxidation, reduction, and hydrolysis.

The control of enzymatic activity by the effect of US is significantly influenced by various intrinsic and extrinsic factors in biocatalysis such as enzyme concentration, substrate concentration, temperature, the pH, and composition of the medium. In some cases of enzyme inactivation using sonication, it is unclear whether the inactivation is solely due to the process of enzyme dissociation into subunits as observed with thermal inactivation. For ultrasonic baths, power is often low to avoid cavitational damage to the tank walls and the power density is reduced due to the presence of large volume or processing liquid. A sudden change in the pressure due to high-power US results in the formation of cavitation bubble which collapses in the subsequent cycle as shown in Fig. 2. This results in the formation of zones having a high localized temperature up to 5000 K along with very high pressure of 50,000 kPa which results in shearing effect. The sonication treatment and the cavitation activity in a sonochemical treatment reactor may vary for the same ultrasound intensity if the sample volume and probe or horn or transducer location is changed. The ultrasound power or energy dissipation to a liquid medium can be expressed in terms of ultrasound power (W), ultrasound intensity (W/cm^2) based on the surface area of irradiation, acoustic energy density (W/mL) based on volume or cavitational intensity. Currently, volumetric acoustic energy density (W/cm^3 or W/mL) has been widely used to indicate ultrasonic power intensity. The measurement of ultrasound amplitude is a much reliable method of indication of the ultrasonic cavitation or ultrasound power. This cavitation intensity can be estimated by measuring hydrogen peroxide (H_2O_2) formation in distilled water during sonication by performing a catalyzed colorimetric procedure reported by Mead et al. [16]. This method can be combined with a calorimetric study carried out during mapping of the sonication reactor as discussed in the further section of ideal protocol for sonochemical biocatalysis. But the determination of H_2O_2 generation during sonication treatment in the enzymatic system is highly complex due to the presence of large molecules of insoluble substrate, including ions and other colloidal components. To date, no reliable method to measure cavitation activity in an enzymatic system has been developed.

3. Ultrasound-assisted enzyme-catalyzed reactions

3.1 Free enzyme catalysis

The US effect on the free enzyme is more vulnerable since there are no diffusion barriers for cavitation to reach the active site of enzyme molecule. It has been reported that ultrasound treatment could enhance the hydrolysis of lignocellulosic biomass [6, 8] which has reduced the time of hydrolysis by twofold while achieving total delignification of 80%. In both studies, free enzyme from the crude broth was used which shows that free enzyme can sustain US waves at low frequency in the range of 24–30 kHz. The temperature control plays a very important role too. There are few more reports on the use of the commercial free form of laccases showing enhanced degradation of ciprofloxacin and

diclofenac [17]. In another study, the influence of ultrasonication on enzymatic hydrolysis of a feedstock was examined. Newspaper, a potential feedstock containing a high level of cellulosic content that can help in the production of bioethanol was treated with ultrasound. The impact of experimental conditions such as temperature, enzyme and substrate loading, power input, and duty cycle on the enzymatic hydrolysis was investigated. The optimized conditions for conventional enzymatic hydrolysis were found to be as follows; temperature (323 K), 5% (w/v) substrate loading, and 0.14% (w/v) enzyme loading. The reaction was incubated for 72 h, and 11.569 g/L of reducing sugar was yielded. On the other hand, for ultrasound-assisted hydrolysis, optimized condition attained were as follows; 3% (w/v) substrate loading, 0.8% (w/v) enzyme loading, power 60 W, and duty cycle (70%). The total yield of reducing sugar, 27.6 g/L was obtained within 6.5 h. These results showed that the ultrasound-assisted enzymatic hydrolysis approach achieved an approximately 2.4-fold rise in the release of reducing sugar concentration. Several other reports are supporting these findings where the synergistic effect of the combination of ultrasound and enzymes was witnessed that lowered the diffusion-limiting barrier to substrate/enzyme binding and ultimately enhanced the rate of reaction [18].

3.2 Immobilized enzyme catalysis

The immobilization of enzyme can increase the thermostability of free form of the enzyme using various immobilization strategies. A purpose of immobilization is to protect the active catalytic site of the enzyme surface. The presence of ultrasound shock waves can severely affect the enzyme structure which may yield a low reaction rate. The reports suggest that the type of enzyme and type of immobilization used present varied impact of US on the overall reaction rate. Cellulase cross-linked aggregates have shown enhanced activity in the presence of low-frequency ultrasound. Magnetic nanoparticles immobilized cellulase when subjected to US had shown an increase in activity by 2- to 3.6-folds activity along with enhanced reaction rate [19]. At the optimized condition of ultra-sonication, that is, 24 kHz frequency, 6 W power and incubation of 6 min, 3.6-fold increase in the activity of the immobilized catalyst over the control experiment were observed. Further, the use of US resulted in the stability of immobilized catalyst as evident by the results. The effect of US has shown to attain hyperactivation of the enzyme by complete unfolding of the active catalytic site which has led to increasing substrate accessibility resulting in enhanced hydrolysis yield. In the case of esterification reaction, immobilized lipase found to be active and followed forward reaction while the use of US prevented backward reaction occurring due to the presence of water. The unfolding of the active site due to US, and the protecting action of immobilized matrix, have led to the progress of reaction thus resulting in higher yield in short span of time. In this case, the reaction of oxidation-reduction was initiated by enzyme but further continued by the effect of radical generation due to transient cavitation.

Ultrasound has been used to intensify some of these esterification reactions. In the esterification reaction of synthesis of citronellol under the solvent-free condition N435 had given conversion over 95% under the US and the enzyme was reused for 5 cycle with a very slight change in activity [20]. Similarly, in the esterification of linoleic acid and ascorbyl acid using tert-butanol, the use of US results in the increase in the yield of ester product to 90% [21]. The *Trametes versicolor* stimulated by US has been immobilized in alginate beads has shown improved catalysis as reported by few authors [10]. Zinc oxide nanoparticles (ZnO) of different morphologies such as nanodisc, nanoflower, and nanorod were prepared and used for the immobilization of horseradish peroxide (HRA) for the removal of phenol via phenol oxidation. The use of US increased the activity of the immobilized and free catalyst to get almost 100% degradation of phenol under the optimized condition in 20 min [9].

3.3 Whole-cell biocatalysis

There are reports of enhanced enzyme production by *T. versicolor* by pulsed exposure of US [10]. The physical effect of increased microconvection and enhanced porosity of cell membrane where the enzyme is stored has led to the release of more enzymes. This increased porosity of membrane has shown to increase substrate consumption by fungi. In case of bacteria, as reported by Balasundaram et al. the release of enzymes takes place from the periplasmic membrane [22] but precaution should be taken to maintain chilling environment or 4°C while performing the sonochemical treatment. This temperature control helps in reducing the loss of enzyme activity due to thermal degradation. The production of the laccase from the alginates beads immobilized mycelia of *T. versicolor* increased after use of US. The optimized conditions for the US treatment were established and resulted in an increase in the production of laccase by twofold than the untreated sample in both the flask and bubble column reactor. The use of US resulted in an improvement in the mass transfer of nutrient, and product between the liquid and gel media. The results were useful and can be used for the large-scale production of laccase using sono-bioreactor [14]. Effect of US and different parameters were studied in detail for the coproduction of uricase and alkaline protease from *Bacillus licheniformis* NRRL14209 [23]. US treatment at 60 W power with 40% duty cycle and 15 min of exposure to fermentation broth after 6 h of growth stage resulted in the maximum yield of 0.825 and 0.646 U/mL of uricase and alkaline protease, respectively. The US treatment increased the yield of uricase and alkaline protease by 1.9–3.8 and 1.2–2.2 times, respectively [23]. In the case of the disruption operation of cells, the mechanical effect is responsible when compared to the chemical effect of the cavitation [24]. The detailed model has shown that each stage of transient cavitation (i.e., expansion, collapse, and the subsequent shock wave of the bubble) may contribute to the membrane permeabilization. The cell disruption by hydrodynamic cavitation and acoustic cavitation was

found to be more selective and energy-efficient method for extraction of periplasmic enzyme compared to the conventional method of cell disruption such as high-pressure homogenizer, bead mill, etc. [22]. The use of hydrodynamic cavitation has been successfully implemented and used for cell disruption and selective release of periplasmic enzymes. Periplasm is the location at which most of the enzymes like alcohol dehydrogenase, proteases, are stored in a cell. The low-frequency sonication by US bath can also bring the same effect if tuned properly. The use of low-frequency and the high-power US resulted in strong cavitation effect that affects the physical, chemical/biochemical, or mechanical properties of the protein. While the use of the low-power and high-frequency US produces very moderate physical effects, this can be used for nondestructive separation and noninvasive analysis of multicomponent mixture. The high-power US resulted in the physical as well as chemical effect in the dairy processing. The physical effects due to cavitation, acoustic irritation, microjetting, acoustic streaming, and shockwave along with chemical reaction including the formation of small amount of highly reactive radicals are used for several applications. However, for enzymatic studies the frequency and power differ from enzyme to enzyme, enzyme molecular weight and structure, reaction to be carried out, and type of medium used.

4. Factors affecting ultrasound-assisted enzyme-catalyzed reactions

In earlier times, apart for cell inactivation, ultrasound played an essential role in disruption and degradation of cell, but in last few decades ultrasound has proven its competence in the enhancement of catalytic activities of enzymes. However, it can be only achieved under optimum biocompatible mild experimental conditions. There are several factors involved in ultrasound treatment that directs the rate of reactions, including the intensity of ultrasound irradiation (input power), ultrasound frequency, the concentration of substrate, the concentration of enzyme, temperature of the system, the effect of polar/nonpolar solvents, and the form of the enzyme (free or immobilized).

4.1 Influence of frequency

As the name suggests, ultrasound waves are mechanical waves producing the frequency (20,000 cycles/s) above the threshold limit of human hearing (16–100 kHz) that can travel through a medium and induct formation of bubbles that eventually grows and bursts [25]. Commercially, three major types of ultrasonic frequencies are available such as power ultrasound (16–100 kHz), diagnostic ultrasound (1–10 MHz), and high-frequency ultrasound (100 kHz–1 MHz) [26]. According to reports, an increase in frequency may significantly diminish the cavitational effect by a negative pressure produced by rarefaction cycle of the sound wave that might not be strong enough in its intensity when combined with the duration. Also, at elevated frequencies compression cycle transpires quicker than the time needed for the microbubble to burst [27]. Moreover, a

further increase in frequencies makes the cavitation zone less violent and almost no cavitation is witnessed thereafter. Hence, power ultrasound frequency can be used to obtain large cavitation bubbles that lead to elevated temperatures and pressures in the cavitation zone [28]. An earlier report examined the effect of ultrasound frequency on the catalytic activity of the cellulase enzyme. It was observed that the activity was enhanced from 6.56% to 10.45% with an increase in a range of frequency (18–16 kHz). This might be due to the positive impact of ultrasound that increased the surface area of the enzyme that ultimately influenced the enzymatic stability resulting in a variation of the catalytic activity. However, as the frequency further increased, a loss of cellulase activity (by 1.02%) was observed due to excessive heat generated by violent collapse of a massive number of bubbles in reaction medium [29]. In another study, the influence of ultrasound frequencies on the catalytic activity of alliinase which was extracted from fresh garlic was investigated. It was recorded that the elevating rates of frequencies (28–100 kHz) at power (0.5 W/cm^2) led to a positive impact on alliinase activity by 47.1% when compared with an untreated enzyme [30]. It was witnessed that the lower frequency-generated bubbles have prolonged expansion cycle when compared to a higher frequency. Also, at a lower rate, several monolayers get evaporated into the bubble whereas at a higher frequency rate, due to lesser expansion time, not even a single monolayer is attained [31]. Therefore, water molecules dissipate more heat during bubble collapse and relatively, at a higher frequency rate, not multiple water molecules form due to short-term expansion [32].

4.2 Influence of intensity/power

Ultrasound intensity is directly influenced by the maximum power input and the operating frequency of the device [33]. As the operating frequency directly influence the ultrasonic power, it is essential to optimize the power input required to get a positive impact on enzyme-catalyzed reaction. Investigation of power in ultrasound treatment is an essential factor to be optimized since it directs the overall course of the reaction. It has been recorded by several researchers that the rate of reaction elevates with an increase in power supply and with further increase in power can lead to a decrease in the rate of reaction after a while [34]. A notable decrease in the rate of reaction with more power input is possible due to the formation of compact clouds of cavitational bubbles in the region around probe that might act as an obstacle to the transmission of energy to the reacting species. Moreover, high power can lead to an increase in bubble formation followed by violent implosion of a substantial number of bubbles and ultimately enhances the rate of reaction [35]. However, prolonged exposure to US is not advised since it may generate excessive heat in the process that can deform the enzyme structure resulting in loss of catalytic activity. Also, more prolonged exposure can adversely affect the life of transducers [36]. The effect of power input of ultrasound was investigated on the activity

of cellulase enzyme and was found to be intensified with an increase in power (up to 15 W). The possible reason for the enhanced activity could be breakage of weak hydrogen bonds along with van der Waals' interactions that lead to a highly active conformation of the enzyme. However, further elevation in the power supply could not enhance the catalytic activity of cellulase [29]. Similarly, in another report, high-intensity ultrasound irradiations show a detrimental impact on the catalytic activity of trypsin. When the level of intensity surpassed optimum value, the activity of the enzyme started decreasing steadily with an increased intensity of ultrasonication [37].

4.3 Influence of pH and temperature

The catalytic activity of the enzyme can be determined to some extent by the microenvironment, where pH and temperature affect the overall rate of reaction to some extent [36, 38]. Temperature plays a crucial role in several heterogeneous reactions where the viscosity of the medium can get highly influenced by temperature and further directs the diffusional rate, which ultimately controls the overall reaction. However, in the case of ultrasonication, temperature exhibits a negative impact and must be optimized to attain a maximum conversion. Nevertheless, the pH and temperature can show a distinct response to the ultrasonication when examined separately. When the effect of pH and temperature were examined for alpha-amylase using central composite design, the impact of temperature was found to be less noticeable when ultrasonication was provided; however, 80% drop in the activation energy was recorded when compared to the study without ultrasound irradiation. Moreover, threefold enhancement in the catalytic activity of alpha-amylase under temperature (up to 40°C) was observed in case of an ultrasound-assisted reaction. Also, an adverse effect on the catalytic activity of enzyme under ultrasonic irradiation was observed due to the pH of media used [39].

4.4 Influence of duty cycle

Enzymes are thermosensitive biomolecules and can be influenced by the mode of ultrasound irradiation employed. Duty cycle is another crucial factor to be monitored and optimized to attain energy-efficient reaction. A duty cycle of the process can be optimized by varying the ON-OFF time of exposure of ultrasound irradiation to the enzyme. The amount of exposure of ultrasound to enzyme directs the extent of structural modification of proteins. Continuous mode is not desirable as a more eminent treatment of irradiation can result in the generation of excessive heat that could quickly and permanently denature the protein in the process [40]. It was witnessed that the lower dose of ultrasound irradiation could help the enzyme to reach maximum activity that can be assigned to incompetent microstreaming generated due to acoustic cavitation. However, the dosage beyond optimized value could end up resulting in a drop in the catalytic activity of enzyme due to unfolding of the enzyme. In a previous study, the effect of duty cycle

was investigated on the activity of β-D-glucosidase. It was observed that the activity of the enzyme was found to be increasing with an increasing duty cycle (33.33%–40%). However, a further increase in duty cycle led to a slight drop in β-D-glucosidase activity. This might be due to the adverse effect of the excessive heat generated by cavitation on enzyme structure at higher duty cycles [41]. Moreover, the continuous mode of ultrasound irradiation can also affect the life of ultrasound transducers since the excessive heat generated by cavitation cannot be entirely dissipated within a short period. In another study, the lipase enzyme from *Candida antarctica* was investigated for the effect of the duty cycle. The maximum catalytic activity was obtained at 0 s on and 5 s off (66.67% duty cycle). Researchers mentioned the possible reason for such observation by relating it with the appropriate influence of impulsive forces on the structure of the lipase enzyme [42]. These reports suggest that power input and irradiation duration primarily affect the overall efficiency of ultrasonication. It also reveals that the excessive and prolonged irradiation of ultrasound can head toward the aggregation of enzymes, thereby, hindering the availability of active sites of protein that ultimately leads to drop in the catalytic activity of enzymes. Therefore, the overall findings support the impact of appropriate duty cycles, power input, and irradiation time on the stability of an enzyme and its catalytic activity.

5. Effect of reactors on enzyme-catalyzed reactions in sonication

5.1 Ultrasonic horn

The dimensions of probe or horn and distance of the tip of horn from the reaction mixture are the most important parameter determining the progress of a reaction. The maximum intensity of energy observed at the tip of the horn. The US horn is not uniform in most cases. Sometimes it may lead to the evaporation of the solvent in the presence of horn. It is only used for intense cavitation processes such as cell disruption for enzyme release from bacterial cells or disinfection of water, as reported by Phull et al. [43]. The radially placed horns are much effective than radially placed probes to achieve uniform cavitational intensities all over the reactor. Most of the enzymes get degraded in the presence of US horn due to its stronger intensity when compared to US probe. Although the setup has a major application in cell disruption studies, not much work has been explored yet [44].

5.2 Ultrasonic bath

Most of the reports show that using an ultrasound bath enhances the activity of enzymes. A part of the enhanced activity is due to the effect of US on the substrate. The increase in relative enzymatic activity in some cases can reach up to 80%. US bath also affects the thermodynamic properties of the enzyme where the energy of activation for the enzyme to act was reduced. The scale-up of US bath design can be done with an increase in the number of transducers placed below the US bath as explained by Gogate et al. [11, 45].

The choice of transducer type is also very important in determining the energy consumption and effectively producing transient cavitation. The arrangement of US transducer has a significant effect on the distribution of shock waves in the sonochemical reactor. Some US reactors have radial transducers which are also effective in case of biocatalysis at higher scales of 10–20 L.

5.3 Ultrasound-assisted packed bed reactor (PBR)

Rotating Packed Bed (RPB) reactor is another type of reactor that has been innovatively designed by several researchers where it is equipped with an ultrasound device [46–48]. In this modified version, ultrasound probes were installed on the top of RPB reactor. This unique arrangement can elevate the mass transfer along with enhanced micromixing in the system. Ultrasound was found to be more sensitive to L-L micromixing over gravity-based (G-L) mass transfer. Since US has established as an efficient means to improve chemical reaction via acoustic cavitation, it was the first report of employing ultrasonication in RPB reactor that enhanced micromixing and mass transfer. Moreover, the influence of reactor-specific factors such as effective interfacial area and mass transfer coefficient (volumetric liquid) concerning micromixing efficiency were compared with and without US assistance and were reviewed orderly. Also, the possible enhancement in RPB reactor concerning micromixing and mass transfer was discussed. The relative segregation index was found to be decreasing by 13.8%, whereas relative mass transfer (volumetric liquid-side) was found to be increasing by 5.5% along with enhancement in the relative effective interfacial area by 3.7%. In another study, intensification of the process was attained by RPB centrifugal force that enhanced micromixing of lipase and substrate. An essential factor that influences mass transfer in RPB is high gravity factor (β). Further, to understand the efficiency of the reactor, at optimal β value, three types of oil were assessed in RPB-assisted hydrolysis system. When the hydrolysis process was analyzed concerning different types of oils, the yields were found to be 15%–25% greater than the yield recorded under conventional continuous stirred tank reactor (CSTR). Also, the reaction time was found to be reduced by 30%–50% that evidently claimed the superiority of RPB reactor over the CSTR system. Other study showed that lipase (*Candida* sp. 99–125) could successfully hydrolyze the oil, heterogeneously using an RPB system. It is to be noted that at optimal high gravity factor ($\beta = 15$), RPB exhibited superior micromixing capability for enzyme and substrate that led to an enhanced hydrolysis yield (93.11%) in 24 h. Therefore, these studies prove that RPB equipped with US can be an efficient candidate biocatalytic hydrolysis [48].

5.4 Scale-up

The sonochemical reactor has been scaled up to 10–20 L with numerous US probes or transducers placed radially [11]. Ultrasonic probes with tuned cylindrical radial have proposed several advantages over ultrasonic probes during inactivation of bacterial strains.

The effectiveness of a radial horn and probe were compared in a study where *Escherichia coli* K12 was inactivated. Further, a finite element model for radial horn and probe was established and predicted parameters of the model were experimentally validated. Also, visual examinations of the extent of cavitation fields generated by both types were assessed. It was observed that radial horn was found to be advantageous over probe as it could produce a highly focused cavitation field with widely dispersed streamers. It was also recorded that with the same amount of power provided to the system, better inactivation of bacterial species *E. coli* K12 was accomplished using a radial horn. Moreover, the radial horn can achieve higher power density that can further enhance the inactivation of microbes while offering uniformly distributed cavitational fields. It can be concluded from these studies that radial horn is comparatively effective than the probe that extends several designing opportunities concerning an in-line flow-through mechanism for process application. A similar device can be used for biocatalysis at a lower frequency while maintaining the same type of setup design. In the case of biocatalysis, transducers can be used radially placed as explained by Gogate et al. [45].

6. Kinetics and thermodynamics of sono-enzymatic synthesis

6.1 Effect of ultrasound on kinetics parameters

In case of an enzymatic reaction, the enzyme has one or more stereospecific active sites for binding of the substrate that involves in the reaction to get the final product [49]. Depending on the size of the molecule, functional group attached to it, stereoselectivity of the molecule, and the size of the active site and enzymes specificity also changes [50]. The primary step in the enzymatic reaction is the formation of a complex between the enzyme and substrate followed by conversion to the desired product. With an increase in the substrate concentration, the activity of enzymes also increases up to specific concentration but remains constant or decreases after a further increase in the concentration of substrate [51]. The decrease in activity or no change in activity is referred as inhibition or poisoning of the active site and it is due to the strong adsorption of the substrate or lack of vacant sites for another reactant of lower concentration. The slow rate of reaction in comparison to chemical catalysis is one of the major disadvantages for enzyme catalysts. Mass transfer limitation due to the structure of enzyme and inefficient mixing of substrates are the main two reasons that exhibit slow reaction rate [52]. The ultrasound induces the physical effects to get micromixing and helps to improve the mass transfer by enhancing active contact between substrate and catalyst. Ultrasound-induced changes in the structure of an enzyme that provides sufficient exposure of the active sites to the substrate and results in a high rate of reaction and overcomes the abovementioned problem.

For the immobilized catalyst, in the absence of the mass transfer resistance, a mathematical model based on initial rate data and Burk-Line weaver double inversion plot can be used. The kinetic model plays a vital role in scale-up and designing of the reactor.

Various research articles and book chapters have given a detailed explanation about the development of the kinetic model for enzymatic reactions [49, 50, 53]. For a single substrate reaction, the most-followed mechanism is based on the Michaelis-Menten kinetic model, while for two or multisubstrate-based reactions, depending on the sequence of the substrate-binding step, mechanism of the reaction is determined [54]. For a two-substrate-based reaction, the mechanism can be based on random substrate binding or ordered substrate binding. In the first case, any of two substrates can bind to the active site, and binding of that first substrate is independent of the second substrate. The Michaelis-Menten constant (K_M) represents affinity of the enzyme toward the substrate, and maximum rate of reaction (V_{max}) are generally calculated by fitting the initial rate of reaction (ν) for each substrate concentration (S) to the Michaelis-Menten equation:

$$\nu = \frac{V_{max}[S]}{K_M + [S]} \tag{1}$$

On further simplification, it can be rewritten as

$$\frac{1}{\nu} = \frac{K_M}{V_{max}} \times \frac{1}{S} + \frac{1}{V_{max}} \tag{2}$$

The values for K_M and V_{max} can be calculated by calculating slope and intercept from the plot of $1/\nu$ versus $1/S$. In the following sections, we have discussed the effect of ultrasound irradiation on the value of K_M and V_{max} and their possible causes.

Muley et al. [55] have studied the effect of ultrasound on K_M and V_{max} value of free cutinase, cutinase immobilized on magnetic nanoparticles (Fe-NPs), and the US-treated free cutinase and cutinase-Fe-NPs, for different concentration of *p*-nitrophenyl butyrate (*p*-NPB). The slight decrease in K_M value of free and immobilized catalyst was noticed after ultrasound treatment indicating enhanced affinity of enzymes toward the substrate. According to the authors, this is due to the change in the structural conformation of the enzyme after treatment resulting in opened and better access to active sites. Further, this also increases in V_{max} value, which confirms that ultrasound treatment improves the catalytic efficiency of cutinase. Similarly, Dabbour et al. [56] have studied the effect of the dual-frequency ultrasound (DFU) treatment on enzymolysis of sunflower meal protein (SMP) using alcalase as a catalyst. The DFU treatment results in the decrease in Michaelis constant K_M by 11.29%, indicating the increase in the affinity among substrate and enzyme. This decrease in the K_M value for DFU pretreatment was possibly due to the modification in the conformation of SMP by a change in monovalent interactions of the enzyme after sonication. Meng et al. [57] have studied the effect of ultrasound treatment on the activity of glucoamylase and its kinetic parameters. The K_M and V_{max} value

were increased under the specified reaction condition of 60°C and ultrasound at 420 W for 10 min. The value of V_{max} increased by 52% at 420 W of ultrasound but decreased with an increase in the power of the US (540 W). Similarly, K_M value was found to be constant for 420 W of ultrasound but decreased with the use of 540 W. This suggests that the low intensity of the ultrasound was beneficial for a kinetic reaction, while further increase in intensity hampered the kinetics of the reaction. In the enzymolysis of tea residue protein (TRP) using alcalase, the K_M value was found to decrease by 32.7% after ultrasound treatment over the control or traditional enzymolysis reaction [58]. The single-frequency countercurrent ultrasound (SFCCU) pretreatment on enzymolysis also resulted in a decrease in V_{max} value by 7.6% in comparison to the traditional or controlled reaction. The use of ultrasound seems to results in the breakage of chemical bonds and hence increases the substrate surface area for an enzyme reaction [59]. A very slight difference in V_{max} of both the process indicates that the highest binding frequency was obtained at the saturation of alcalase by the substrate. In ultrasound-assisted solvent-free enzymatic alcoholysis for the synthesis of monoglyceryl phenolic acids, the value of K_M and V_{max} was found to increase by fourfold and fivefold, respectively [60]. The lipase (Novozyme 435) catalyzed reaction was found to have enhanced activity under the ultrasound treatment as compared to the traditionally stirred system [61]. In the sequential dual-frequency ultrasound (SDFU)-assisted enzymolysis of rapeseed protein by alcalase as a model enzyme, the values of K_M was found to decrease by 17.61% in comparison with conventional reaction [61]. The reason behind the decrease in the K_M value was explained based on the change in the enzyme conformation as described above.

In the enzymolysis of corn gluten meal (CGM) catalyzed by immobilized alcalase, the effect of triple-frequency ultrasound (TFU) on kinetics parameters were studied, and K_M value was found to decrease by 27% in comparison to control reaction [62]. The decrease in the K_M value was explained based on conformational changes in the enzymes due to the ultrasonic cavitation. Further, the use of ultrasound results in shock waves and the generation of free radicals which destroys the formation of starch-protein conjugate and thus increases the protein surface area and hence increases the chance of protein and enzyme contacting [63]. Wang et al. [64] have studied the effect of ultrasound on the hydrolysis of starch using glucoamylase and calculated the kinetics parameters. The V_{max} value was found to be increased by 25.87% while the value of K_M decreased by 45% with the use of the ultrasound. The improved mass transfer and the change in the conformation change resulting in the better affinity were the main reason for the seen changes in parameters. Effect of ultrasound on activities of pectinase (PE), xylanase, and cellulase was measured in terms of K_M and V_{max} [65]. In the case of pectinase, ultrasound decreased the K_M by 20%, proposing a better enzyme-substrate affinity while V_{max} value was found to be constant. For xylanase (XLN), the K_M value was the same for the ultrasound and mechanical stirring (MS), but the V_{max} value increased due to sonication. While the V_{max} value for cellulase (CE) was also increased by 37.5%. The increase in the

V_{max} indicates the enhancement of the reaction. In the case of PE, sonication caused structural changes and thus increased the activity, whereas in the case of CE and XLN, ultrasound affected the substrate chains and thus increases the activity by providing easy access to the active sites. Jin et al. [66] have studied the effect of the use of multi-frequency power ultrasound (MPU) on the enzymolysis of CGM, and the kinetics parameters were also calculated. The results indicated that use of MPU resulted in the decrease in the K_M value by 26.1% in comparison to the conventional method and this was possibly due to the increased affinity between substrate an enzyme stimulated by the ultrasound. The same kind of effect was observed in the cellulase catalyzed carboxymethyl cellulose hydrolysis under ultrasound irradiation [67]. Under the power intensity of 17.33 W/cm^2 for the hydrolysis reaction, the K_M value was decreased by 17%, and the V_{max} value was increased by 34% in compassion to the untreated sample. The use of ultrasound resulted in the conformational changes in the cellulase structure and thus increased the overall affinity of the substrate. Souza et al. [39] have found a significant effect of ultrasound on the kinetic parameters calculated at two different temperature for amylase. Under the use of ultrasound, V_{max} value increased with increase in temperature whereas K_M value remained constant. Further in the absence of the ultrasound, K_M value decreased significantly by 65% at a higher temperature while V_{max} increased up to 190% with temperature. Suliiman et al. [68] also investigated the effect of ultrasound treatment on the kinetic parameters of cellulase. They found the enhanced catalytic activity of cellulase and increase in the V_{max} value and slight decrease in K_M value. However, the affinity of the enzyme was improved as compared to the control experiment, which is due to structural change in the enzyme. The effect of ultrasound on kinetic parameters associated with glucose oxidase was explored with respect to time [69]. The increase in the irradiation time has a negative effect as the turnover number of enzyme and V_{max} value decreases with increase in time up to 60 min. Also, it resulted in a stepwise decrease of approximately 50% in the K_M values as compared to the fresh enzyme. For a short time irradiation, V_{max} increased with time, which was possibly due to a physicochemical change in the enzyme. Further increase in the irradiation time resulted in a significant difference in structure and hence resulted in a decrease in the activity [69].

From the above discussion, the ultrasound enhanced activity of the enzyme in most of the cases, and it is reflected in terms of the decrease in the constant K_M value and sometimes increase in the V_{max} value. The change in this value can be explained based on the following points: (1) Use of ultrasound results in cavitation, and this results in a shear force, intense pressure, and temperature, which changes the enzymatic kinetic parameters that give higher affinity to the substrate, which results in an enhanced rate of formation of product and hence, the K_M value decreases while V_{max} increases. (2) Use of ultrasound results in the additional turbulence and results in the enhanced mass transfer phenomena and thus, the reaction rate increases [70] and it results in the decrease in the K_M value with increased V_{max} [70].

6.2 Effect of ultrasound on thermodynamic parameters

Effect of ultrasound on the activation energy (E_a) and other thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) are analyzed to understand the microscopic effect of ultrasound irradiation on the enzyme. The activation energy is the minimum amount of energy required to initiate the reaction to form the product and for most of the reaction, it ranges from 40 to 400 kJ/mol [71]. The reaction progresses very rapidly if activation energy is lower than 40 kJ/mol. Enthalpy (ΔH) refers to the total heat content of the system, if the change in enthalpy is positive, the reaction is endothermic in nature, and a lower enthalpy means it requires less energy. In the enzymatic reaction, ΔH depends on the capacity of formation and disruption of the chemical bond and structure of enzyme used [72]. In the enzymatic reaction, ΔG refers to the energy difference between the complex of substrate binding with the enzyme at the ground state and the complex of substrate binding with the enzyme at activated state [73]. The low value of ΔG indicates that substrate conversion to the product was more feasible [74]. Entropy (ΔS) of the system represents the degree of disorder between transition state and ground state of reaction, and it is related to a number of a molecule with sufficient energy to react [75]. Also, with an increase in temperature, the activity of enzymatic complexes enhances. The increase in temperature results in more energy supply, which helps to overcome the minimum activation energy and results in high collision frequency, thus helps to get a high initial rate of reaction. It is well observed that with an increase in temperature, the enzymatic activity increases up to certain temperature and after that further increase in temperature results in a decrease in activity due to inactivation of enzymes. Several literature and papers have been published to cover the general method of calculation of these parameters and are described herein short.

For calculation of activation energy for any catalyst, the rate constant (k) at different temperature was calculated and used to make a linear plot of k of rate constant per second against the temperature, according to Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \tag{3}$$

Enthalpy (ΔH) can be calculated using the activation energy as per Eq. (4),

$$\Delta H = E_a - RT \tag{4}$$

Gibbs free energy (ΔG) can be calculated using Eq. (5) and using the above-calculated value ΔS can be calculated using Eq. (6).

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta G}{RT}\right) \tag{5}$$

where T is the absolute temperature (K), h is Planck constant (6.6256×10^{-34} J/s) and $k_B$is Boltzman constant (1.38×10^{-23} J/K).

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

Similarly, thermodynamic parameters, ΔG, ΔS, and ΔH can be calculated using the Eyring's transition state theory from a plot of $\ln k/T$ against $1/T$ (Eq. 7).

Combining Eqs. (5) and (6) we have

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta G}{RT}\right) = \frac{k_B T}{h} \exp\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right)$$

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H}{RT} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S}{R} \tag{7}$$

Dabbour et al. [56] have calculated the activation energy for enzymolysis of SMP using alcalase enzyme and was found to be 31.49 and 23.89 kJ/mol for control and the ultrasound treated the reaction, respectively. The decrease in E_a value shows that the ultrasound-treated reaction requires less energy and results in the faster reaction between enzyme and substrate. Further, the effect of DFU treatment on other thermodynamic parameters was also studied. The ΔH and ΔS value decreased 26.13% and 9.10% of controlled reaction values, respectively. Further, the positive ΔH value indicates that the reaction is endothermic. The decrease in ΔS value confirms the improved affinity among the substrate and enzyme, which can be due to the enhancement in binding affinity among substrate and enzyme due to the more orderly distribution of enzyme and substrate after ultrasound treatment in the reaction. The ΔG value increased with an increase in temperature for both US-treated and control reaction. However, in the case of the ultrasound-treated reaction, the increase rate in ΔG was higher in comparison with the control reaction. The thermodynamic properties such as E_a, ΔH, ΔS in the enzymolysis of TRP was found to be decreasing by 8.5%, 9.0%, and 8%, respectively, with the use of ultrasound while ΔG was increased in comparison to the traditional enzymolysis [58]. As a result of sonication and thermal effect, the protein structure of the enzyme was modified that helped to drive the reaction faster and thus E_a and ΔH value were decreased. The activation energy of the zein hydrolysis reaction using an angiotensin-converting enzyme (ACE) was calculated for control reaction and compared with the E_a value of sweeping frequency ultrasound (SFU)-treated enzyme [76]. The E_a value for SFU pretreated and traditional hydrolysis reaction was calculated to be 39.06 and 48.55 kJ/mol, respectively. The lower E_a value confirms the ultrasound treatment affects the catalytic rates. Further, the value of ΔH for SFU-treated reaction decreased by 20.63% when compared to traditional reaction, indicating that ultrasound treatment favored the formation of the substrate enzyme complex and a transition state. The value of ΔS also decreased by 6.16% with SFU treatment indicating the reduced disorder after treatment. The decrease in the above two parameters also resulted in a decrease in the value of ΔG

by 7.02%. The change in all these parameters is mainly due to a change in the structure of the substrate. The effect of ultrasound pretreatment on whey protein enzymolysis was studied, and results were compared with the control reaction [77]. The activation energy, enthalpy, and entropy of whey protein enzymolysis were found to be decreasing by 15.9%, 16.8%, and 16.4% respectively. However, the Gibbs energy was almost constant. This change was mainly due to increases in the surface-free sulfhydryl content and an increase in surface hydrophobicity caused by the US-induced unfolding of whey protein. Gawas et al. [78] have studied the effect of ultrasound treatment on the thermodynamics property of solvent-free synthesis of ethyl laurate from ethanol and lauric acid using fermase as a catalyst. The E_a values for the reaction was found to be 20.95 and −23.92 kJ/mol for conventional and ultrasound-assisted reaction, respectively. The negative value of activation energy indicates that the reaction is spontaneous. The values of ΔH and ΔS were also found in negative as compared to the conventional reaction system. This further confirms the spontaneous nature of the esterification reaction under ultrasound treatment. In the rapeseed protein enzymolysis catalyzed by alcalase, the thermodynamic parameters such as, ΔH, ΔS, and E_a were reduced after SDFU treatment as compared to the conventional method by 31.78%, 18.0%, and 29.56%, respectively [61] while, the SDFU had minimal effect on ΔG value of the reaction [61]. A decrease in the E_a after SDFU treatment indicates the decrease in the energy barrier for the reaction and thus reaction processes at a faster rate with a low amount of energy. The altered protein structure of the enzyme and the enhanced affinity between enzyme and substrate due to the SDFU treatment were the main factors for change in the ΔH and ΔS value. Thermodynamic parameters such as E_a, ΔH, and ΔS were found to be decreased by 17.1%, 15.2%, and 24.1%, respectively, in TFU-assisted enzymolysis reaction of corn gluten meal. The positive change caused by the ultrasound in the protein conformation, secondary structure, and microscopic structure has resulted in a decrease in these thermodynamic parameters [62]. Similar kind of change in thermodynamic parameters was also seen in the hydrolysis of the starch by glucoamylase [64]. The E_a value was decreased by 12.5%, which resulted in a low-energy barrier and thus, the reaction could progress at a higher rate and lower temperature. The values of other parameters like ΔH and ΔS were also decreased; however, the ΔG value had no significant change.

The activation energy value for PE was almost same for the ultrasound and mechanical stirring (MS) system while for CE and XLN, E_a value was high in comparison to the MS system even though the activity was improved under the ultrasound as discussed above [65]. The activation energy was calculated based on rate constant obtained for the particular enzyme used in the reaction and even though the E_a value were high but the difference in the activity of CE and XLN were also high under the ultrasound, which indicates that the activity of CE and XLN were more affected by ultrasound bath's temperature. The value of Gibbs free energy (ΔG) was almost equal for PE and XLN and lower for CE under the ultrasound in comparison to MS. Further, the ΔH value for PE

was decreased by 5.7% which indicates that conformational change in the PE structure and thus giving high activity. Whereas for CE and XLN, the high difference in the activity of theses catalyst under the ultrasound in comparison with MS by an increase in temperature shows no change in ΔH for ultrasound and MS. The activation energy for the ultrasound-assisted hydrolysis of waste cooking oil (WCO) using immobilized lipase (Novozyme 435) under solvent-free condition were calculated under the optimized condition and compared with the conventional method [79]. In comparison to the conventional stirring method, use of ultrasound resulted in a decrease in the E_a value of reaction. The combination of ultrasound and continuous stirring have further resulted in a decrease in the E_a value to get −20.79 kJ/mol. The negative value suggests the enhanced mass transfer and decreased energy barrier that resulted in the high reaction rate under ultrasound treatment. In the enzymolysis of CGM by alcalase, the thermodynamic parameters such as E_a, ΔH, and ΔS were decreased by 23%, 24.3%, and 25.3%, respectively, under the treatment of ultrasound [66]. Sudhedar et al. [67] have found the similar kind of effect on the thermodynamic properties of cellulase catalyzed hydrolysis of carboxymethyl cellulose. The values of different parameters such as E_a, ΔS, ΔH, and ΔG were found to be reduced by 64.7%, 37.3%, 68%, and 1.3%, respectively, in comparison to the nontreated samples. In the enzymolysis of defatted wheat germ protein catalyzed by alcalase, thermodynamic parameters were calculated and compared with the conventional method [80]. The values for different parameters like E_a, ΔS, ΔH, and ΔG were decreased by 68.6%, 1.4%, 74%, and 34.3%, respectively. This exponential decrease in the thermodynamic parameters was mainly due to the conformational changes in the enzyme structure caused by the breakage of hydrogen bonds and aggregation of the protein [80]. The similar type of decrease in the thermodynamic parameters for the different enzymatic reaction was also seen for lipase, alcalase, and α-amylase catalyzed reaction under the ultrasound [71, 81–83].

The decrease in activation energy of reaction after ultrasound treatment refers that the enzymatic reaction can occur very easily due to the lower energy barrier to catalyze the reaction. In general, ultrasound treatment of enzyme results in the change in enzyme conformation, and hence the enzyme activity enhances, which results in a decrease in ΔG value [84, 85]. Also, the value of enthalpy (ΔH) decrease after ultrasound treatment and is possibly due to the modification in the structure of the enzyme (sometimes referred to as conformational changes) caused by the breakdown of noncovalent bonds. As explained by Ma et al. [86], the oxidative modification of amino acid residues and the initiation of cross-linking and aggregation also results in improved enzyme activity. The enhanced activity of enzyme also leads to an increase in the spontaneity of reaction as indicated by the higher ($-\Delta S$) values for some enzymatic treatment at the atmospheric process [86]. Further, the use of ultrasound results in the microturbulence and acoustic waves due to sonication that increases static pressure and hydrodynamic stresses that help to the breakdown of weak linkages like hydrogen, vander Waal's bond and electrostatics, etc.

The use of ultrasound results in the enhancement in the activity of the enzymatic reaction, and it is represented or reflected by the change in the kinetic parameters such as K_m and V_{max} along with a change in thermodynamic parameters. These changes are generally compared with conventional methods to see the effect of the ultrasound. Table 1 provides a summary of the effect of the ultrasound on the different parameters when compared to the conventional method.

Table 1 Effect of US treatment on the kinetic and thermodynamic parameter in comparison to the conventional process.

Enzyme	Application	Type of US device/optimum condition	Effect on kinetic and thermodynamic parameters	Ref.
Fe-NPs immobilized cutinase	Hydrolysis of *p*-nitrophenyl butyrate	Ultrasonic bath sonicator, 24 kHz,7.63 W	K_M and V_{max} value increase for the free as well as immobilized enzymes	[55]
Alcalase	Enzymolysis of sunflower meal protein	Dual-frequency ultrasound, 20/40 kHz, 220 W/L power	K_M, E_a, ΔH, ΔS, were decrease by 11.29%, 24.13%, 26.13%, and 9.10% with slight increase in the ΔG	[56]
Glucoamylase	Hydrolysis of starch	The ultrasonic reactor, 40 kHz,420 W power	K_M and V_{max} value increased after US treatment while E_a, ΔH, and ΔG decreased with a slight increase in ΔS	[57]
Alcalase	Enzymolysis of tea residue protein	Single-frequency countercurrent ultrasound, 20 kHz, 377 W/L power	K_M, V_{max}, E_a, ΔH, and ΔS value decreases by 32.7%, 7.6%, 8.5%, 9.0%, and 8%, respectively, while ΔG increased slightly under the US	[58]
Lipase	Alcoholysis for the synthesis of monoglyceral phenolic acids	Microtip probe, 20 kHz, 250 W power	Fourfold and fivefold increase in the K_M and V_{max}	[60]

Continued

Table 1 Effect of US treatment on the kinetic and thermodynamic parameter in comparison to the conventional process—cont'd

Enzyme	Application	Type of US device/optimum condition	Effect on kinetic and thermodynamic parameters	Ref.
Alcalase	Enzymolysis of rapeseed protein	Sequential dual-frequency ultrasound, 150 W/L, 201–40 kHz	K_M value decreased by 17.61%. E_a, ΔH, and ΔS values decrease by 29.56%, 31.78%, and 18%, respectively, with negligible effect on ΔG	[61]
Immobilized alcalase	Enzymolysis of corn gluten meal	Triple-frequency ultrasound, 20/28/40 kHz, 150 W/L	K_M value decreased by 27% along with a decrease in E_a, ΔH, and ΔS values by 17.1%, 15.2%, and 24.1%, respectively, with no significant effect on ΔG	[62]
Glucoamylase	Starch hydrolysis	ultrasonic horn, 22 kHz, 7.20 W/mL	Increase in V_{max} value by 25.87% while K_M, E_a, ΔH, and ΔS values decrease with no significant effect on ΔG	[64]
Pectinase	Hydrolysis of Pectin	Ultrasonic bath (300 × 240 × 150 mm), 40 kHz, 220 W	K_M and ΔH value decreased with no significant change in V_{max}, E_a, and ΔG	[65]
Xylanase	Hydrolysis of xylan	Ultrasonic bath (300 × 240 × 150 mm), 40 kHz, 220 W	V_{max}, E_a value increased with no significant change in K_M, ΔG, and ΔH values	[65]

Table 1 Effect of US treatment on the kinetic and thermodynamic parameter in comparison to the conventional process—cont'd

Enzyme	Application	Type of US device/optimum condition	Effect on kinetic and thermodynamic parameters	Ref.
Cellulase	Hydrolysis of cellulose	Ultrasonic bath ($300 \times 240 \times 150$ mm), 40 kHz, 220 W	V_{max}, E_a value increased with no significant change in K_M and ΔH values. ΔG value decreased in comparison to conventional stirring	[65]
Alcalase	Enzymolysis of corn gluten meal	Multifrequency power ultrasound using sweeping frequency and pulsed ultrasound bath (362 mm × 294 mm × 502 mm), 28/68 kHz, 80 W/L	K_M value decreased by 26.1%. E_a, ΔH, and ΔS values decreased by 23%, 24.3%, 25.35% with a slight change in ΔG value	[66]
Cellulase	Carboxymethyl cellulose hydrolysis	Cylindrical horn (probe sonicator), 20 kHz, 17.33 W/cm^2	V_{max} value increased by 34% while K_M, E_a, ΔH, ΔS, and ΔG were reduced by 17%, 64%, 68%, 37.3%, and 1.3% respectively	[67]
Amylase	Hydrolysis of starch	Ultrasonic bath, 40 kHz, 132 W	Under the US, V_{max} value increased with increase in temperature whereas K_M value remained constant	[39]
Cellulase	Hydrolysis of cellulose and carboxymethyl cellulose	Ultrasonic horn-type reactor ($d = 12.7$ mm), 20 kHz, 11.8 W/cm^2, duty cycle 10%	Enhancement in V_{max} by 85% while K_M reduced to 47% of control reaction	[68]
Glucose oxidase	Oxidation of glucose	Ultrasonic horn-type reactor ($d = 9.5$ mm), 23 kHz	K_M value reduced by 50% while, V_{max} increase for a short time of irradiation	[69]

Continued

Table 1 Effect of US treatment on the kinetic and thermodynamic parameter in comparison to the conventional process—cont'd

Enzyme	Application	Type of US device/optimum condition	Effect on kinetic and thermodynamic parameters	Ref.
Alcalase	Casein hydrolysis	Ultrasonic horn-type reactor ($d = 2$ cm), 20 kHz, 80 W	E_a, ΔH, ΔS, and ΔG were reduced by 70.0%, 75.8%, 34.0%, and 1.3%, respectively	[71]
Alcalase	Hydrolysis of zein	Sweeping frequency ultrasonic bath reactor (362 mm × 294 mm × 502 mm), 40 kHz, 600 W	Values of E_a, ΔH, ΔS, and ΔG decreased by 19.54%, 20.63%, 6.16%, and 7.02%, respectively, under the US	[76]
Alcalase	Hydrolysis of whey protein	Ultrasonic horn-type reactor ($d = 1.5$ cm), 20 kHz, 300 W	Values of E_a, ΔH, and ΔS decreases by 15.9%, 16.8%, 16.4% respectively, with no significant change in ΔG under the US	[77]
Immobilized lipase fermase	Synthesis of ethyl laurate	Ultrasonic bath (300 × 150 × 150 mm), 25 kHz, 100 W, 50% duty	Negative E_a value along with a decrease in the ΔH and ΔS value. No significant change in ΔG after US treatment	[78]
Immobilized lipase	Hydrolysis of waste cooking oil	Ultrasonic bath reactor (300 × 150 × 150 mm), 22 kHz, 100 W, duty cycle 50%	Values of E_a, ΔH, and ΔS were negative with no significant change in ΔG after US treatment	[79]
Alcalase	Defatted wheat germ protein enzymolysis	Ultrasonic horn-type reactor ($d = 2$ cm), 20 kHz, 600 W	E_a, ΔS, ΔH, and ΔG were decreased by 68.6%, 1.4%, 74%, and 34.3%, respectively	[80]

Table 1 Effect of US treatment on the kinetic and thermodynamic parameter in comparison to the conventional process—cont'd

Enzyme	Application	Type of US device/optimum condition	Effect on kinetic and thermodynamic parameters	Ref.
Immobilized lipase	Hydrolysis of *p*-nitrophenyl acetate	Ultrasonic horn-type reactor ($d = 3.5$ cm), 22 kHz, 15.48 W/cm^2, duty cycle 66.67%	Thermodynamics properties lowered due to US treatment	[81]
Alcalase	Hydrolysis of porcine cerebral protein	Ultrasonic horn-type reactor ($d = 2.0$ cm), 20 kHz, 80 W	Values of E_a, ΔH, and ΔS decreases by 76%, 82%, and 31%, respectively, with no significant change in ΔG under the US	[82]
α-Amylase	Hydrolysis of starch	Ultrasonic bath, 40 kHz, 100 W	E_a value decreased by 60% under US	[83]
Amylo-glucosidase	Hydrolysis of starch	Ultrasonic bath, 40 kHz, 100 W, duty cycle (50%)	E_a value decreased by 40% under US	[83]

7. An ideal sonochemical protocol for biocatalysis

Considering several factors affecting the overall efficiency of ultrasound-assisted biocatalysis, an ideal protocol for a desired reaction can be developed. However, a thorough understanding of these parameters followed by implementation in the process is vital. Nevertheless, to attain an ideal protocol for specific ultrasound-treated biocatalysis, the following factors should be considered.

7.1 Selection of reactor vessel

The glass test tubes or reactors made up of glass of uniform thickness are preferred so that energy dissipated is uniform and reaches throughout the reaction medium. Usually, stainless steel or metal reactor is avoided since there are reports of enzyme inactivation due to high mechanical impact. Moreover, corrosion or pitting in ultrasound bath on the surface of reactors can occur. Shape geometry of US reactor plays a very important role since energy dissipated depends on the surface thickness of the reactor used. Beaker or test tube can also be used with wall with uniform thickness for carrying out sonochemical biocatalysis. For small volumes of reactions, in case of test tubes, a stirrer is not required but for larger volumes, a stirrer can be used for uniform distribution of content and ultrasound waves. Also, stirrers provide reproducible results if the cavitation intensity is uniformly maintained.

7.2 The medium

Distilled water is being used as a medium in ultrasound treatment that avoids interactions of ions resulting in generation of heat to obtain reproducible results. The ultrasound bath is preferably filled with distilled water to avoid corrosion and interactions of ions to minimize the effect on the temperature of bath. Most of the enzymatic reactions are carried out in an aqueous medium; however, in some cases such as lipase-catalyzed reaction, it may be carried out in an oily medium or organic solvent. In such cases, calorimetric studies for control solvent should be preestimated. The mapping study can also be carried out in advance with the solvent or liquid medium to be used.

7.3 Mapping

The first step in sonochemical biocatalysis is to map the ultrasound bath or probe. The ultrasound bath has to be characterized for acoustic power dissipation using calorimetric measurement [87, 88]. The location of the reactor has a major influence on reaction progress due to difference in cavitational intensity in different zones of US reactors. The major hurdle in implementation or scale-up of sonoreactors is to obtain uniform cavitation intensity. The distance of the bottom of the vessel from the transducer is also important and should be varied and studied in details during mapping.

7.4 Bath type

In the case of US bath, the enzymatic studies can sustain until 37 kHz. The operational range of Frequency can be considered from 20 to 37 kHz. Researchers have used 25 kHz in studies of laccases and amylase [87]. However, the range of frequency for ultrasound probe sonicator will differ from the bath.

7.5 Placement of reactor

Location of placement of enzyme solution in a sonicator bath is also one of the important governing factors that influence the overall efficiency of the process. The location of transducers also affects the cavitational intensity or energy dissipation (energy dispersed throughout the reaction mixture). In the case of US bath, the location of the transducer and the number of transducers affects the cavitational intensity. So, in such cases mapping of the US bath plays an important role. The fixed reactor or test tube containing a known quantity of enzyme solution is placed at different locations in a US bath [87, 88]. Moreover, the position and shape of the vessel has a significant impact on extraction yield the same is the case of enzymatic reactions to be carried out in US bath. Several other studies [87] showed that distance of 2.54 cm above the bottom of the bath, 7 cm diameter of flat bottom vessel, 6.35-cm liquid height, 122-W input power and 25 kHz frequency showed maximum extraction yield.

7.6 Enzyme form

The enzyme used should be soluble in its optimum buffer and temperature (at room temperature). Ultrasound waves can be uniformly distributed thus affecting uniform effect on enzyme and substrate molecules. Most of the free enzymes are soluble in the aqueous phase which is influenced significantly by US.

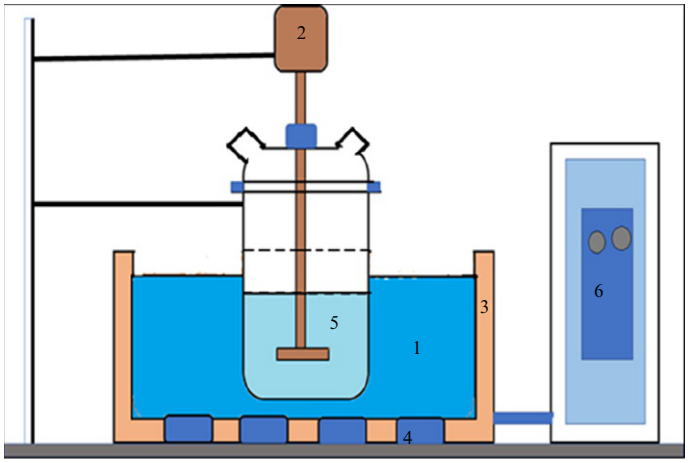

Fig. 3 Schematic representation of ultrasound bath with experimental setup used in sonochemical biocatalysis studies (recommended design) ((1) water, (2) overhead stirrer, (3) ultrasound bath, (4) transducers, (5) reaction mixture, and (6) ultrasound controller).

7.7 Temperature control

The temperature in US bath should be able to control using thermocouples, where at required temperature circulating cooling water through a coil immersed in the ultrasound bath can be provided. Alternatively, a stirrer can be introduced in US bath as shown in Fig. 3. The location of transducers in the diagram is also the most widely used design. There are designs available for US bath acting as both US bath and functions as water bath with variable frequency and power Input. In the case of usage of test tubes, there should be a provision of the stirrer in the ultrasound bath outside the test tubes to circulate water to achieve uniform temperature.

7.8 Monitoring enzyme activity concerning time

The basic stability study of control enzyme has to be carried out without substrate at optimum pH and temperature conditions. The timely samples should be removed and checked for the presence of enzyme activity at different frequency and power. The time duration till which a particular concentration of enzyme can sustain US should be studied in detail.

8. Conclusion and future prospects

Ultrasound has been used in various industries for the enhancement in productivity via process intensification. Apart from process intensification, ultrasound also offers several other advantages over conventional methods such as the reduction in waste generation, comparatively safer operation, low-energy requirement, and material usage. However, the excessive usage of ultrasound may hinder the overall efficiency of the process, and there is an urgent need to define the specific protocols to get the maximum out of this advanced technique. Several kinds of work have been published and discussed in recent past and have been discussed here to understand the effect of various experimental parameters to attain the optimum utilization of ultrasonication. Moreover, it was observed that appropriate ultrasonication with agitation resulted in an intense enhancement in the catalytic activity of the enzyme where it helped sound waves to distribute uniformly. The other parameters, such as duty cycle and operating temperature also affect the overall conversion of the reactant. One of the critical parameters is US power that drastically affects the enzyme structure and may result in enhanced activity, but if provided above the threshold level, might decrease with time. Therefore, it is essential to define the power, time, duty cycle, operating temperature, and degree of agitation to get the ideal protocol for the optimized use of ultrasound. Further, the kinetics and thermodynamics studies have shown that for the particular condition or the defined protocol of the ultrasonication, the enzyme can be stable and more active than the conventional method. For the kinetics parameters, decrease in the values of K_M and an increase in the value of V_{max} reflect the enhancement in the activity of the enzymes. While in the term of thermodynamic parameters, decrease in the activation energy (E_a), enthalpy (ΔH), entropy (ΔS) indicates the stability of the active catalyst. However, the primary problem with the ultrasound has been its scale-up to attain large-scale production as the construction of the big ultrasound bath or horn is not economically feasible until we tackle the problems related with higher noise and energy dissipation. Also, a successful implementation of ultrasound on the industrial scale majorly has the gap between the data from lab scale to pilot plant and followed by lack of usual relations between the obtained data for the final commission of plant. Detailed and rigorous research is needed to get these data along with the optimization of the design of the process. Also, studies have to be more focused toward obtaining the data and establish effective relationships between the parameters at the lab and industrial scale. To conclude, the use of the ultrasound is beneficial for most of the reactions of biocatalysis and only fruitful if the usage is based on the optimized protocol. The several parameters which constitute an ideal protocol are needed to be studied in detail to get the optimized ultrasound parameters, based on that a protocol for a desired reaction and condition can be defined.

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CHAPTER 7

Sonochemical protocol for coupling reactions

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1 Introduction and background

With the advent of "green chemistry" to promote sustainable chemical reactions, the quest for environmentally clean technology and alternative energy sources became a research field of interest to many researchers, as a result of which ultrasonic irradiation along with ball milling and microwave irradiation were evolved as techniques that could add value to the conventional laboratory setup [1]. Although initial reports on the physical, biological [2], and chemical effects [3] of ultrasound were published long way back in 1927 [4], there was only modest activity in this field in the next 50 years [5]. Chemists started getting interest in this field only after Fry et al. published their work of reducing α,α′-dibromo ketones using ultrasonically dispersed mercury in protic solvents in 1978 [6], which is signified by a fair number of reports published in the following years [7–14]. The term "sonochemistry" slowly made its entry into chemical literature to describe chemical events induced by ultrasound and the first symposium fully devoted to sonochemistry was staged by the Royal Society of Chemistry Annual Congress held at Warwick University, UK during 8–11 April 1986 [15]. The field has thereafter been continuously enriched by many contributors across the globe and numerous review articles have been found published till date describing the evolvement of the field [1, 15–24]. Although these reviews summarize the overall progress of the application of ultrasound in chemical synthesis, however, to the best of our knowledge, not a single such report is available in the literature that concentrate solely on sonochemical protocol for coupling reactions.

Coupling reactions have always been of immense importance in organic chemistry as they constitute an unassailable tool for joining two fragments of the same, similar, or different substrates in organic synthesis. Although in recent years, scientific studies have been found to be more focused on metal catalyzed name coupling reactions, viz., Suzuki cross-coupling, Kumada cross-coupling, Sonogashira cross-coupling, Negishi cross-coupling, Stille cross-coupling, Buchwald-Hartwig cross-coupling, etc., the term

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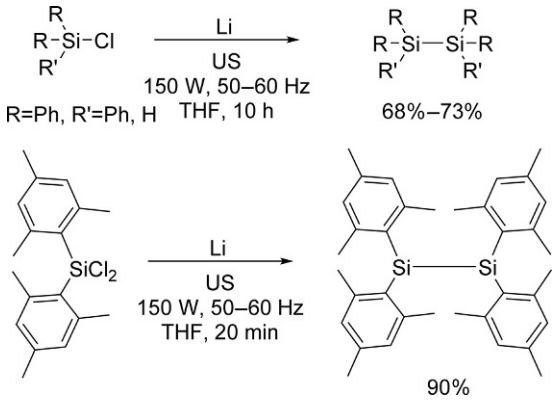
"coupling reactions" does not restrict to these only and signifies a much broader area. In a wider perspective, any organic reaction that leads to new C—C and/or C—X (X is elements other than C, for example, O, N, Si, etc.) bond formation falls under the coverage of organic coupling reactions. The simplest example includes Aldol-condensation reaction in which two carbonyl compounds join via a new C—C bond formation under alkaline condition. One of the classical electrophilic aromatic substitution reactions, the diazo-coupling was so named as there occurs coupling of diazonium compound with an electron-rich aromatic system via a new C—N bond formation. Many classical name reactions viz. the Grignard reaction, Barbier reaction, Refortmatsky reaction, etc., which have been discussed under the heading of nucelophilic addition reaction to carbonyl groups in textbooks are varied types of coupling reactions. So, there remains only a few types of organic reactions, viz., oxidation, reduction, elimination, etc. which do not come under the coverage of coupling reactions. As a result, it becomes quite challenging and a huge task to prepare a comprehensive review on "sonochemical protocol for coupling reactions" and is beyond the scope of a single chapter in a book. This chapter encompasses the sonochemical methodologies developed for organic coupling reactions carried out in the presence of metal species only. The metal species may sometimes be used in stoichiometric amounts, while many times are used in catalytic amounts. A few other chapters of this book have been dealing with the sonochemical protocol for coupling reactions which are carried out in absence of metal species under different headings.

2 Sonochemical coupling reactions

Literature reports suggest that Luche et al. reported the first sonochemical coupling reaction in 1980 by carrying out reductive coupling of organic halides (mainly bromides) with carbonyl compounds in the presence of Li wire or Li-2% Na sand (4 equiv.) [8]. They performed the reaction using an ultrasound laboratory cleaner (60 W, 50 kHZ) and made a particular note that the Barbier reaction could be done in wet technical grade THF under their setup within 10–40 min. Plenty of reports have been published afterwards demonstrating the application of ultrasonic irradiation in varied classes of coupling reactions, which will be discussed in the following section. However, two research works by Boudjouk et al. are worth mentioning here as those cannot be placed under any of the subheadings below. These two reports describe ultrasound-promoted Si—Si coupling reactions of chlorosilanes [10] and dimesityldichlorosilanes [12] in the presence of Li wire in the THF to yield disilanes with Si—Si single and Si—Si double bond, respectively (see Scheme 1).



Scheme 1 Ultrasound-induced coupling of chlorosilanes in the presence of Li. *Credit: P. Boudjouk, B.H. Han, Organic sonochemistry. Ultrasound promoted coupling of chlorosilanes in the presence of lithium wire, Tetrahedron Lett. 22 (1981) 3813 and P. Boudjouk, B.-H. Han, K.R. Anderson, Sonochemical and electrochemical synthesis of tetramesityldisilane, J. Am. Chem. Soc. 104 (1982) 4992.*

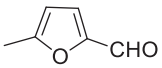
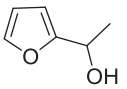
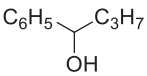
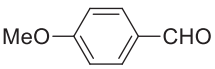
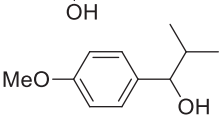
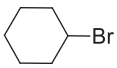
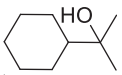
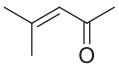
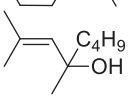
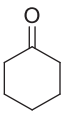
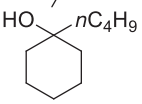
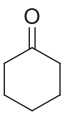
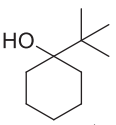
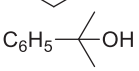
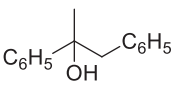
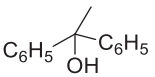
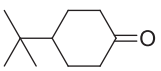
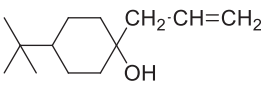
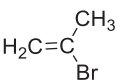
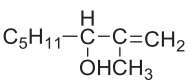
2.1 Sonochemical protocol in C—C coupling reactions

2.1.1 Reductive coupling to carbonyl (>C═O) functionality under ultrasonic irradiation

As mentioned earlier, the first report of sonochemical coupling reaction demonstrated modified Barbier reaction between organic halides and carbonyl compounds in the presence of Li species [8]. Ultrasonic irradiation afforded the preparation of organolithium species in situ, which readily reacted with the carbonyl compound in a subsequent step. Although typical reactions of organolithium species demand dry solvents under an inert atmosphere, they were successful to get products in high yield using technical grade THF under ambient reaction conditions (see Table 1). Authors accounted such high efficiency of their reaction protocol either to the alterations occurred at the metal surface during sonication or its ability to keep the metal surface free from derived species (organolithium, lithium halide, or hydroxide) so that it remains highly activated during the entire course of the reaction. Subsequent to this, they performed a study to understand the mechanism of the effect of ultrasonic irradiation on reaction rate and yield of the sonochemical Barbier reaction by carrying out reactions between benzaldehyde, *n*-heptyl bromide, and Li-wire in dry THF [25]. They examined the metal surface using electron microscopy at different time intervals and made a remark that acoustic waves formed during ultrasonication has important activation role through the cavitation phenomenon. As the key step in Barbier reaction has been the single electron transfer (SET), they mentioned that the ultrasonic waves have direct effect on the SET. Lee et al. extended the scope of Barbier-type coupling reactions for the synthesis of homopropargyl alcohols

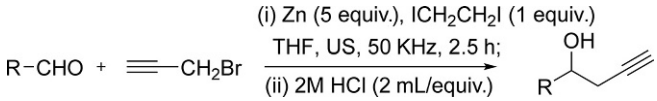
under ultrasonic irradiation starting from 3-bromo-1-propyne and carbonyl compounds in the presence of Zn (5 equiv.) and 1,2-diiodoethane (1 equiv.) in THF (Scheme 2).

Table 1 Modified Barbier reaction under ultrasonic irradiation.[a]

Entry	R-X	Carbonyl compound	Product	Reaction time (min)	Yield[b]
1	Me-I			10	100
2	*n*-C_3H_7Br	C_6H_5-CHO		10	100
3	*n*-C_3H_7Br			15	100
4	*n*-C_4H_9Br	$(n\text{-}C_4H_9)_2C{=}O$	$(n\text{-}C_4H_9)C{-}OH$	15	100
5				30	80
6	*n*-C_4H_9Br			15	100
7	*n*-C_4H_9Br			15	84
8	*t*-C_4H_9Br			30	76
9	C_6H_5Br			30	100
10	$C_6H_5CH_2Br$	$C_6H_5{-}COCH_3$		10	95
11	C_6H_5Br	$C_6H_5{-}COCH_3$		30	92
12	$CH_2{=}CH{-}CH_2Br$			15	76
13		$C_6H_5{-}CHO$		40	96
14	$CH_3{-}CH{=}CH{-}Br$	$C_5H_{11}{-}CHO$	$C_5H_{11}{-}CHOH{-}CH{=}CH{-}CH_3$	40	95

[a]Reaction condition: A flask containing a 0.1-M ethereal solution of an alkyl or aryl halide in the presence of Li wire or Li-2% Na sand (4 equiv.) was irradiated in the water bath of an ultrasound laboratory cleaner (60 W, 50 kHz).
[b]The yields were calculated with respect to the initial carbonyl compound from VPC measurements.
Credit: J.-L. Luche, J.-C. Damiano, Ultasounds in organic syntheses. 1. Effect on the formation of lithium organometallic reagents, J. Am. Chem. Soc. 102 (1980) 7926.

They synthesized 15 numbers of homopropargyl alcohols from both aldehydes and ketones; however, ketones generated low contamination of allenyl alcohols [26].



Scheme 2 Synthesis of homopropargyl alcohols via sonochemical Barbier-type reaction. *Credit: A.S.-Y. Lee, S.F. Chu, Y.T. Chang, S.H. Wang, Synthesis of homopropargyl alcohols via sonochemical Barbier-type reaction, Tetrahedron Lett. 45 (2004) 1551.*

In 1982, Boudjouk et al. reported the advantages of carrying out the Reformatsky reaction under ultrasonic irradiation over conventional procedures (see Table 2) [13]. While high yield and short reaction time were the main features of their work, the methodology also enabled to eliminate the need of preparing Zn powder by reduction of a Zn-salt using metallic K in refluxing THF under argon atmosphere [27] as well as the use of trimethyl borate [28].

Table 2 Comparison of yields and reaction times for Reformatsky reaction.

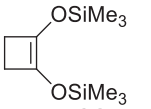
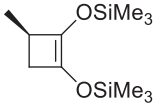
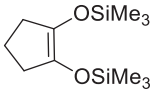
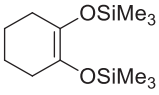
		Yield, %; reaction time for $RR'C(OH)CH_2CO_2Et$		
Entry	**$RR'C{=}O$**	**Sonically accelerated**	**Activatedzinc powder[a]**	**$(MeO)_3B$-THF solvent[b]**
1	$R = C_3H_7$; $R' = H$	90; 5 min[c] 94; 2.5 h[d]	97; 1 h	90; 5 h
2	$R = C_7H_{15}$; $R' = H$	100; 5 min[c] 100; 2.5 h[d]	78; 1 h	
3	$R = C_6H_5$; $R' = H$	98; 5 min[c] 98; 5 [d]	98; 1 h	95; 12 h
4	Cyclopentanone	98; 30 min[c] 97; 3 h[d]	97; 1 h	87; 5 h

[a]Reaction condition: $RR'CO$(0.058 mol), $BrCH_2CO_2Et$ (0.060 mol), Activated Zn powder (0.065 mol), diethylether (40 mL), −5°C, positive nitrogen pressure.
[b]Reaction conditions: $RR'CO$ (100 mmol), $BrCH_2CO_2Et$ (100 mmol), $(MeO)_3B$ (25 mL), THF (25 mL) Zn metal (6.4 g, 100 mg-atoms), 25°C, static nitrogen pressure.
[c]Reaction condition: $RR'CO$ (1 mol), $BrCH_2CO_2Et$ (1.2 mol), Zn(1.8 mol), KI (0.20 mol) dioxane, 25–30°C, ultrasonication (150 W, 50/60 Hz).
[d]Reaction conditions: $RR'CO$ (1 M), $BrCH_2CO_2Et$ (1.2 M), Zn (3.0 M), KI (0.84 M), 25–30°C, ultrasonication (150 W, 50/60 Hz).
Credit: B.-H. Han, P. Boudjouk, Organic sonochemistry. Sonic acceleration of the Reformatsky reaction, J. Org. Chem. 47 (1982) 5031.

Salaün et al. developed a sonochemical protocol for intramolecular acyloin coupling of 1,4-, 1,5-, and 1,6-carboxylic esters to 4-, 5-, and 6-membered ring products in the presence of cholorotrimethylsilane in THF-containing metallic Na at 0°C to ambient temperature [29]. Typical condition demands highly dispersed sodium for the reaction

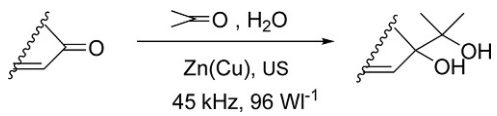
to happen which was significantly simplified and improved by this sonochemical version as Na could be used in small cubic pieces (5-mm edge) and refluxing toluene was excluded as solvent, yet delivering the products in a yield comparable to conventional procedures (Table 3).

Table 3 Comparison of yields of acyloin-coupling reaction.

Entry	Esters	Products	Yields (%) under ultrasonic condition (time)[a]	Yields (%) under conventional condition (Source)
1			82 (2 h)	78–81 (K. Ruhlmann et al. Chem. Ber. 1967, 3820)
2			80 (2 h 30 min)	78 (J. Salaun et al. Tetrahedron 1989, 45, 3151)
3			85 (1 h 45 min)	93 (K. Ruhlmann, Synthesis 1971, 4, 256)
4			83 (1 h 45 min)	89 (K. Ruhlmann, Synthesis 1971, 4, 256)

[a]Reaction conditions: Ester (30 mmol), $ClSiMe_3$ (180 mmol), Na (1.2 equiv.), THF (40 mL), 0–5°C, ultrasonication (60 kHz, 80–160 W).
Credit: A. Fadal, J.-L. Canet, J. Salaün, Ultrasound-promoted acyloin condensation and cyclization of carboxylic esters, Synlett 2 (1990) 89.

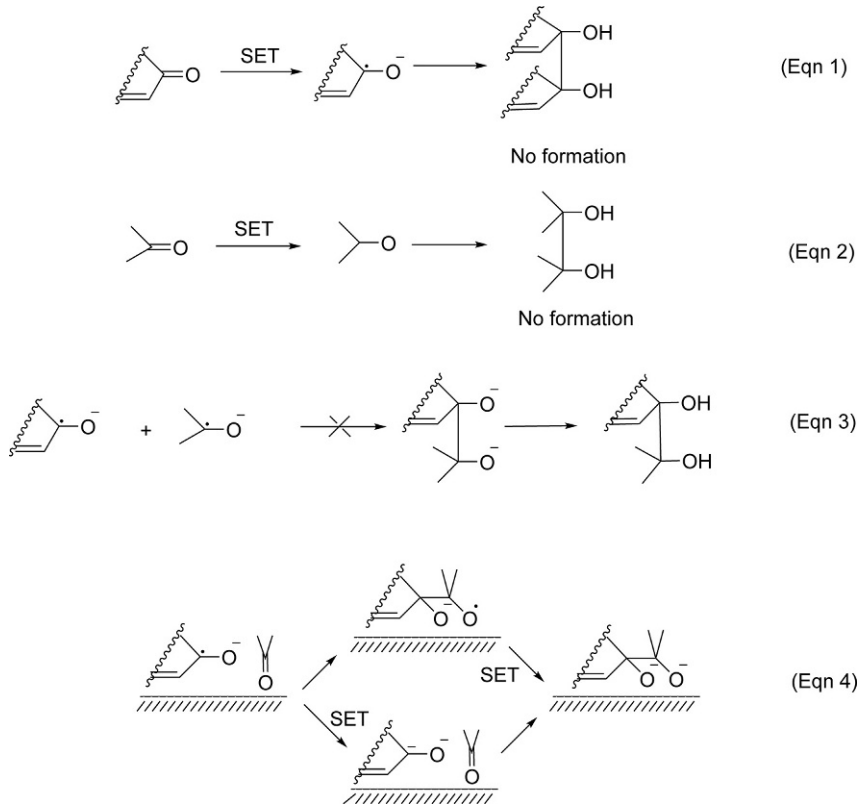
Luche et al., the pioneer research group of sonochemical coupling reactions also worked on pinacol reductive coupling reaction under ultrasonic irradiation [30]. They developed a reductive cross-coupling protocol for α,β-unsaturated carbonyl compounds to acetone in the presence of Zn—Cu metallic couple in a 4:1 (v:v) acetone-water mixture, which resulted the coupling product with unprecedented ease (Scheme 3). Zn—Cu



Scheme 3 Sonochemical cross-coupling between enones and acetones. *Credit: P. Delair, J.-L. Luche, A New Sonochemical carbonyl cross-coupling reaction, J. Chem. Soc. Chem. Commun. 20 (1989) 398.*

couple was prepared in situ from Zn dust and $CuCl_2$ dihydrate under sonication and the addition of enone was done after the formation of the metal couple and the sonication was continued for 90 more minutes. No self-condensation products of the carbonyl

compounds were observed while no reaction occurred at the conjugate position of the enone (Eqs. 1 and 2, Scheme 4). The absence of 2,3-dimethyl-butane-2,3-diol, the self-condensation product of acetone (Eq. 2), ensured that the final product was not formed via free radical coupling of the two ketyl radicals (Eq. 3, Scheme 4). These observations



Scheme 4 Mechanistic study and the plausible mechanism for Scheme 3. *Credit: P. Delair, J.-L. Luche, A new sonochemical carbonyl cross-coupling reaction, J. Chem. Soc. Chem. Commun. 20 (1989) 398.*

led them to suggest that SET occurs only at the more easily reducible carbonyl group, that is, at enone, but not at acetone. However, they did not disclose any reason of not detecting the self-condensation product of the enone. They proposed a mechanism in which the radical anion of enone either reacts with acetone to give an unstable radical that undergoes rapid stabilization by a second SET or it first undergoes reduction to generate a dianion followed by reaction with acetone (Eq. 4, Scheme 4). They could not acquire enough evidence to conclusively comment on the preferred route between these two.

T.-s. Li et al. too contributed to sonochemical pinacol coupling by carrying out coupling of aromatic aldehydes with ketones using Mg in aqueous NH_4Cl at room temperature [31].

2.1.2 Sonochemical C—C coupling in the presence of Li species

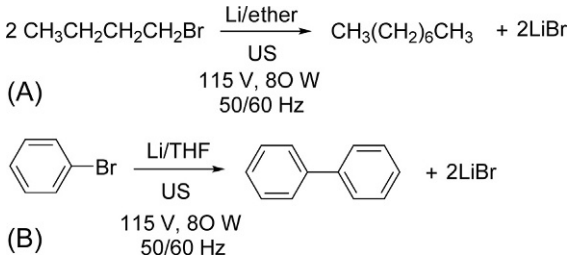
The first report on sonochemical direct C—C coupling was published in 1981 by Boudjouk et al. [11], a research group who had been focusing on sonochemical Si—Si coupling reaction during that period [10, 12]. They carried out coupling of various organic halides in the presence of Li-wire under sonication (see Table 4) and commented that little or no reaction occurred in absence of sonic waves. Reactions with entry no. 1–6 of Table 4 are examples of Li-promoted Wurtz-Fittig reaction, while reactions with entry nos. 7 and 9 are Li promoted Wurtz reactions. Impressed by this work, Lash et al. designed two undergraduate laboratory experiments [32], one for the synthesis of

Table 4 Ultrasound-induced coupling of organic halides with Li-wire.

Entry	R—X	Product[a]	Time (h)	Yield (%)
1	C_6H_5Cl	$C_6H_5—C_6H_5$	12	70
2	C_6H_5Br	$C_6H_5—C_6H_5$	10	70
3	C_6H_5I	$C_6H_5—C_6H_5$	12	73
4	p-$CH_3C_6H_4Br$	(p-$CH_3C_6H_4$)$_2$	10	52
5	p-$CH_3C_6H_4I$	(p-$CH_3C_6H_4$)$_2$	10	42
6	m-$CH_3C_6H_4Br$	(m-$CH_3C_6H_4$)$_2$	10	36
7	$C_6H_5CH_2Cl$	$C_6H_5CH_2CH_2C_6H_5$	40	60[b]
8	C_6H_5COCl	$C_6H_5C(=O)—C(=O)C_6H_5$	17	73
9	$CH_3CH_2CH_2Cl$	$CH_3(CH_2)_6CH_2$	17	72

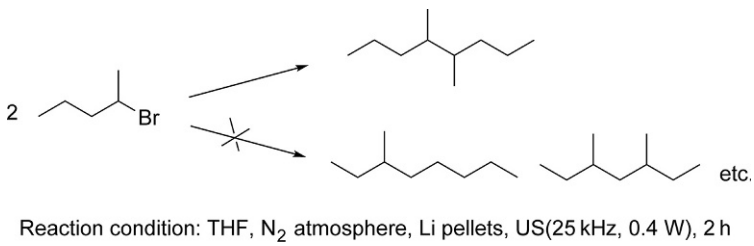
[a]Reaction condition: R—X (0.02 mol), Li wire 1/4″ × 1/8″ (1 equiv.), dry THF (5 mL), ultrasonication (117 V, 150 W, 50/60 Hz).
[b]Yield from NMR. All others are isolated yield.
Credit: B.H. Han, P. Boudjouk, Organic sonochemistry. Ultrasound-promoted coupling of organic halides in the presence of lithium wire, Tetrahedron Lett. 22 (1981) 2758.

n-octane by Wurtz reaction and another for biphenyl synthesis by Wurtz-Fittig reaction in the presence of Li-wire under sonication simply by adding more conventional workup procedures to the original methodology (Scheme 5). Osborne et al. attempted to extend the methodology for coupling of heteroaryl bromides [33]. While 3-bromopyridine, as expected, resulted 3,3′-bipyridine albeit in low yield (the main reaction was debromination of 3-bromopyridine); 2-bromopyridine produced three isomeric bipyridines: 2,2′-bipyridine (65%), 4,4′-bipyridine (30%), and 2,4′-bipyridine (5%). The formation of three isomeric dimers was in contrast to the basic concept of Wurtz-type reaction where the new bond normally forms at positions previously occupied by halogen atoms and thus



Scheme 5 Li-promoted sonochemical procedure for *n*-octane and biphenyl. *Credit: T.D. Lash, D. Berry, Promotion of organic reactions by ultrasound: Coupling of alkyl and aryl halides in the presence of lithium metal and ultrasound, J. Chem. Edu. 62 (1985) 85.*

implied that the mechanism was not that of the Wurtz-type coupling. They investigated more examples of heteroaryl halides in their subsequent report and proposed a mechanistic pathway for the unusual formation of 4,4′-bipyridine from 2-bromopyridine [34]. Price et al. too worked on sonochemical Wurtz-type coupling reactions to acquire more information on their mechanism, however, ended with the demonstration of involvement of radical intermediates only in the reaction [35]. The same group later worked on sonochemical Wurtz coupling of alkyl bromides and reported that the coupling is regiospecific and takes place at C-atoms attached to the halogen atom in the starting organic bromide (Scheme 6) [36]. So, the reaction led to single isomer formation which was in contrast to earlier observations with aryl halides. They accounted it to their low stability in comparison to their aryl counterpart due to which alkyl radicals undergo coupling rapidly to result the dimer prior to the formation of any secondary radical. They extended the methodology to dibrominated alkyls, which produced low molecular weight oligomers and also cited examples of alkyl-aryl coupling under similar conditions.



Scheme 6 Li-promoted regiospecific sonochemical Wurtz coupling of 2-bromopentane. *Credit: D. Vandenburg, G.J. Price, Ultrasound promoted Wurtz coupling of alkyl bromides and dibromides, Ultrason. Sonochem. 19 (2012) 7.*

2.1.3 Sonochemical C—C coupling in the presence of Pd species

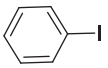
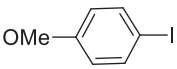
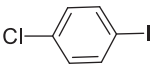
Most of the modern day coupling reactions involve Pd catalysis: Heck reaction, Sonogashira coupling, Stille coupling, and Suzuki coupling are to name a few. Development

of ultrasonic protocols for these important coupling reactions have been attempted by various research groups at different point of times and so a plethora of reports have been found published in journals of repute. The following subsections will deal with sonochemical C—C coupling in the presence of Pd species under different headings.

Sonochemical Heck coupling

The first report on ultrasound-promoted Heck reaction was published by Srinivasan et al. (2001) [37], in which iodobenzene and substituted iodobenzene were described to react with alkenes/phenylacetylene in various ionic liquids at ambient temperature (30°C) with considerably enhanced reaction rates (Table 5). A divalent Pd-complex was formed

Table 5 Heck reaction of iodobenzenes with activated alkenes/alkyne under sonication in $[bbim]^+ Br_2/[bbim]^+ BF_4$.[a]

No.	Aryl halide	Olefin/alkyne	Time/h	Product	% Yield[b] (isolated)
1		Methyl acrylate	2.0	Methyl cinnamate	81
		Ethyl acrylate	1.5	Ethyl cinnamate	87
		Styrene	1.5	Stilbene	82
		Phenylacetylene	2.0	Diphenylacetylene	78
2		Methyl acrylate	3.0	4-Methoxymethyl cinnamate	82
		Ethyl acrylate	3.0	4-Methoxyethyl cinnamate	79
		Styrene	3.0	4-Methoxystilbene	80
		Phenylacetylene	2.0	4-Methoxyphenyl) phenyl acetylene	77
3		Methyl acrylate	1.5	4-Chloromethyl cinnamate	79
		Ethyl acrylate	1.5	4-Chloroethyl cinnamate	77
		Styrene	1.5	4-Chlorostilbene	73
		Phenylacetylene	2.0	4-(Chlorophenyl) phenyl acetylene	78

[a]Reaction conditions: Iodoarene (2 mmol), alkene/alykyne (2.1 mmol), sodium acetate (0.2 g), $Pd(OAc)_2$ (0.02 mmol), ionic liquid (1.5 mL), Ar atmosphere, ultrasonication (50 kHz).
[b]Yields are based on iodobenzenes.
Credit: R.R. Deshmukh, R. Rajagopal, K. V. Srinivasan, Ultrasound promoted C—C bond formation: heck reaction at ambient conditions in room temperature ionic liquids, Chem. Commun. 1 (2001) 1545.

in situ which was evident from NMR and MS studies (Fig. 1). They postulated that the Pd-complex underwent in situ reduction to zero-valent Pd species in the subsequent step, which was accelerated by electron transfer reactions under sonochemical condition

by cavitation phenomenon. They accounted it to the enhanced reaction rate of their methodology. They carried out in situ TEM analysis to investigate the formation of Pd nanoparticles and reported Pd-cluster formation during the process. Very recently,

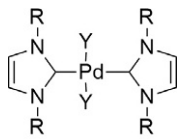
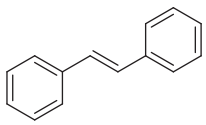
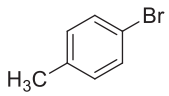
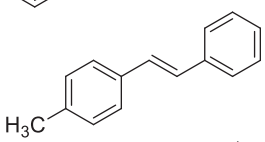
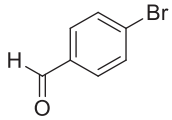
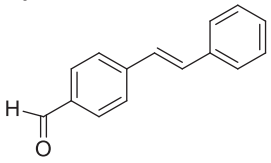


Fig. 1 Divalent Pd-complex formed during Heck reaction of iodobenzenes with activated alkenes/alkyne under sonication in $[bbim]^+$ Br_2/$[bbim]^+$ BF_4. *Credit: R.R. Deshmukh, R. Rajagopal, K.V. Srinivasan, Ultrasound promoted C—C bond formation: Heck reaction at ambient conditions in room temperature ionic liquids, Chem. Commun. 1 (2001) 1545.*

Naeimi et al. developed $NiFe_2O_4$@TASDA-Pd(0) as a highly active and reusable catalyst for Heck coupling reaction in DMF under ultrasonic irradiation [38]. They carried out comparative studies of the product yield and time requirement of the reactions under thermal as well ultrasonic condition, and observed a comparable high yield in significantly low reaction time in the later (see Table 6).

Table 6 Mizoroki-Heck cross-coupling of aryl halides and styrene in the presence of $NiFe_2O_4$@TASDA-Pd(0).[a]

Entry	Aryl halide	Product	Thermal conditions[b] Time (h)/ yield[d] (%)	Ultrasonic conditions[c] Time (min)/ yield[d] (%)
1			4/96	8/99
2			5.5/87	10/95
3			6/90	12/96

Continued

Table 6 Mizoroki-Heck cross-coupling of aryl halides and styrene in the presence of $NiFe_2O_4$@TASDA-Pd(0)—cont'd

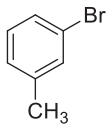
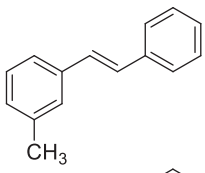
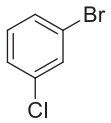
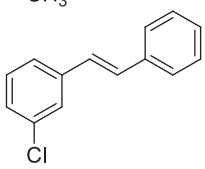
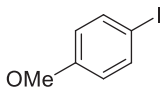
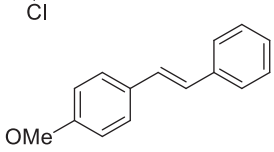
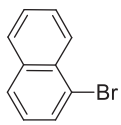
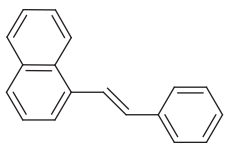
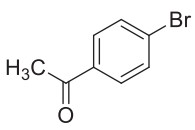
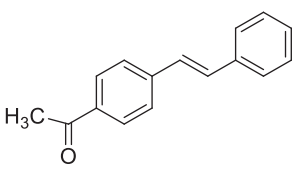
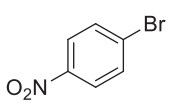
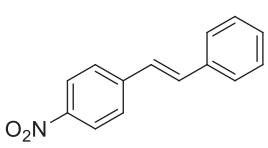
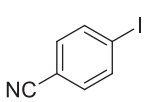
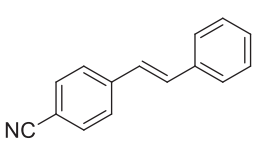
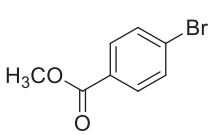
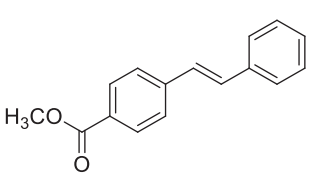
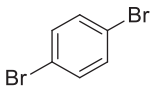
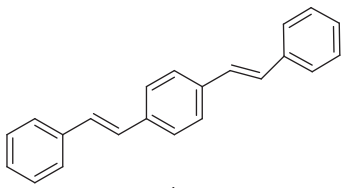
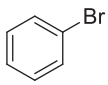
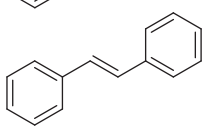
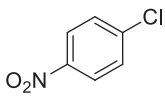
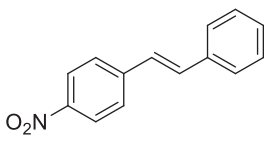
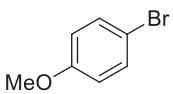
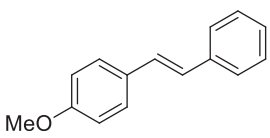
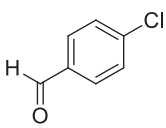
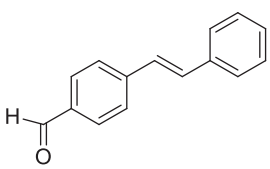
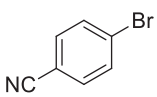
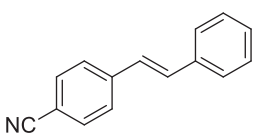
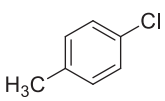
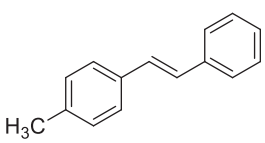
Entry	Aryl halide	Product	Thermal conditions Time (h)/yield (%)	Ultrasonic conditions Time (min)/ yield (%)
4			5/81	9/94
5			7/87	14/95
6			3/78	6/92
7			8/72	14/92
8			7/91	13/94
9			6/94	12/98
10			2.5/95	5/98
11			7/80	15/93

Table 6 Mizoroki-Heck cross-coupling of aryl halides and styrene in the presence of $NiFe_2O_4$@TASDA-Pd(0)—cont'd

Entry	Aryl halide	Product	Thermal conditions Time (h)/yield (%)	Ultrasonic conditions Time (min)/ yield (%)
12			7/90	14/93
13			7/85	12/93
14			10/66	25/65
15			9/83	16/87
16			11/65	30/63
17			8/80	13/90
18			12/51	35/58

[a]Reaction conditions: Aryl halide (1 mmol), styrene (1.2 mmol, for entry 12, 2.2 mmol), amount of catalyst (0.02 g) and NEt_3 (2 mmol) in DMF.
[b]At 130°C.
[c]Applied power: 45 W.
[d]Isolated yield.
Credit: H. Naeimi, F. Kiani, Magnetically thiamine palladium complex nanocomposites as an effective recyclable catalyst for facile sonochemical cross coupling reaction, Appl. Organomet. Chem. 33 (2019) 9–10.

Sonochemical Suzuki coupling

The first report on ultrasound-promoted Suzuki cross-coupling was published by Srinivasan et al. [39], the same research group who first reported sonochemical Heck coupling reaction too [37]. As a continuation to their studies on sonochemistry in ionic liquids, they extended their reaction protocol for Heck reaction with a slight modification to Suzuki cross-coupling reaction of halobenzene and phenylboronic acid at ambient temperature (30°C) in [bbim][BF_4] using MeOH as a cosolvent (see Table 7). From Table 7, it is very clear that the methodology was successful to carry out coupling of phenylboronic acid with various halobenzenes including chlorobenzenes, which are normally less or nonreactive. Like their earlier work, they proposed the formation of a divalent Pd-complex as a precursor to the active catalyst, the zero valent Pd species.

Table 7 Suzuki cross-coupling reaction of halobenzenes with phenylboronic acid in [bbim]$^+$[BF_4]$^-$/MeOH under ultrasonic irradiation.[a]

No.	Substrate	Time/min	Yield of biaryls (%)
1	Iodobenzene	20	92[b]
2	4-Methoxyiodobenzene	20	93[c]
3	4-Chloroiodobenzene	30	85[b]
4	4-Nitroiodobenzene	30	82[c]
5	Bromobenzene	45	82[b]
6	4-Methoxybromobenzene	10	85[c]
7	4-Nitrobromobenzene	20	90[c]
8	Chlorobenzene	60	42[b]
9	4-Nitrochlorobenzene	30	65[c]
10	4-Chlorotoluene	60	52[b]
11	2,4-Dinitrochlorobenzene	90	42[c]

[a]Reaction condition: Aryl halide (0.5 mmol), phenylboronic acid (0.5 mmol), [bbim][BF4] (0.5 g), $Pd(OAc)_2$ (0.001 g), NaOAc (0.045 g) [NaOMe (0.035 g) for chlorobenzenes], MeOH (1 mL), Ar atmosphere, ultrasonication (50 kHz).
[b]Based on GC analysis with external standards.
[c]Isolated yields by column chromatography.
Credit: R. Rajagopal, D. V. Jarikote, K. V. Srinivasan, Ultrasound promoted Suzuki cross-coupling reactions in ionic liquid at ambient conditions, Chem. Commun. 6, 616, 20,002.

Cravatto et al. reported Suzuki homocoupling of arylboronic acids under high-intensity ultrasound in neat water using Pd/C as recyclable heterogeneous catalyst system in the absence of added ligands [40]. They demonstrated successful homocoupling of 19 numbers of different aryl and heteroaryl boronic acids under their reaction condition. In 2008, Wu et al. developed the methodology for Suzuki cross-coupling reaction in water using cyclopalladated ferrocenylimine catalyst systems (Fig. 2) [41]. They carried out the reactions under both conventional heating and ultrasonic irradiation and the results are summarized in Table 8. Table 8 clearly reflects the advantage of carrying out the reactions under ultrasonic irradiation both in terms of reaction time and resultant yields.

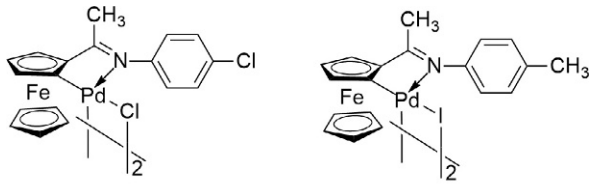


Fig. 2 Cyclopalladated ferrocenylimine catalyst systems employed by Wu et al. *Credit: J. Zhang, F. Yang, G. Ren, T.C.W. Mak, M. Song, Y. Wu, Ultrasonic irradiation accelerated cyclopalladated ferrocenylimines catalyzed Suzuki reaction in neat water, Ultrason. Sonochem. 15 (2008) 117.*

Table 8 Ultrasonic irradiation and conventionally heated Suzuki coupling of aryl halides with phenylboronic acid in water.

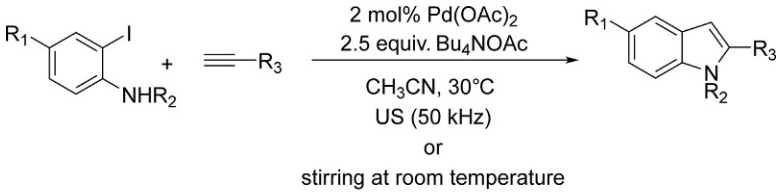
		Ultrasonic irradiation with heating (70°C)			Conventional heating (100°C)		
Entry[a]	Aryl halides	Reaction time (h)	Catalyst loading (mol% Pd)	Yields	Reaction time (h)	Catalyst loading (mol% Pd)	Yields
1[b]	PhI	1	0.5	94[c]	5	0.5	100[c]
2[b]	PhI	0.5	1	93[c]	3	1	100[c]
3[b]	4-$CH_3OC_6H_4I$	1	1	86[c]	20	1	83[c]
4[b]	PhBr	3	0.5	73[c]	6	0.5	100[c]
5[b]	4-$CH_3OC_6H_4Br$	1.5	1	75[c]	20	1	95[c]
6[b]	4-$CH_3OCC_6H_4Br$	2.5	1	96[c]	4	1	94[c]
7[b]	2-$CH_3C_6H_4Br$	3	1	83[c]	10	1	88[c]
8[b]	4-$CH_3OC_6H_4Cl$	8	1	Trace	40	1	13[d]
9[b]	3-$NO_2C_6H_4Cl$	8	1	<5[d]	18	1	24[d]
10[b]	4-$NO_2C_6H_4Cl$	8	1	30[c]	24	1	57[c]
11[e]	4-$NO_2C_6H_4Cl$	8	1	80[c]	24	1	86[c]
12[e]	4-$CH_3OCC_6H_4Cl$	8	1	75[c]	24	1	82[c]
13[e]	2,4-$N_2O_4C_6H_3Cl$	7	1	96[c]	10	1	96[c]
14[e]	2,4-$N_2O_4C_6H_3Cl$	7	0.1	94[c]	10	0.1	91[c]

[a]Reaction stoichiometry: PhX (2.0 mmol), $PhB(OH)_2$ (3.0 mmol), K_3PO_4 (4.0 mmol), H_2O 13 mL, catalyst, TBAB for conventional heating (2.0 mmol).
[b]Cat. 1 was used and TBAB as emulsifying agent for conventional heating.
[c]Isolated yields based on ArX.
[d]Average results of two runs determined by GC based on ArX.
[e]Cat. 2 and TBAB as emulsifying agent were used.
Credit: J. Zhang, F. Yang, G. Ren, T.C.W. Mak, M. Song, Y. Wu, Ultrasonic irradiation accelerated cyclopalladated ferrocenylimines catalyzed Suzuki reaction in neat water, Ultrason. Sonochem. 15 (2008) 117.

Sonochemical Sonogashira coupling

An early report of sonochemical Sonogashira coupling has been found published by Srinivasan et al. (2005) in which they demonstrated copper and ligand-free coupling of a variety of aryl halides (both bromides and iodides) with terminal acetylenic compounds

in acetone as well as room-temperature ionic liquid 1,3-di-*n*-butylimidazolium tetrafluoroborate ([bbim]BF_4) [42]. They ascertained the role of ultrasound in generating the active catalyst (Pd(0) nanoparticles) as well as promotion and enhancement of catalytic activity of the species in the reaction. In the subsequent year, they developed a sonochemical methodology for 2-substituted indoles via tandem Sonogashira coupling 5-*endo-dig* cyclisation as shown in Scheme 7 [43]. They carried out the reactions under both silent condition and ultrasonic irradiation and observed product formations in the same range; however, the time requirement of the reactions was hugely reduced by



R_1 = H, CH_3, CO_2Me, COMe
R_2 = Ts, Ms
R_3= Ph, p-tolyl, 4-methoxy phenyl, 3-fluoro phenyl, naphthyl, 1-hydroxy ethyl

Scheme 7 Synthesis of 2-substituted benzo[*b*]furan under ultrasonic irradiation *Credit: S.S. Palimkar, P. Harish Kumar, R.J. Lahoti, K. V. Srinivasan, Ligand-, copper-, and amine-free one-pot synthesis of 2-substituted indoles via Sonogashira coupling 5-*endo*-dig cyclization, Tetrahedron 62 (2006) 5111.*

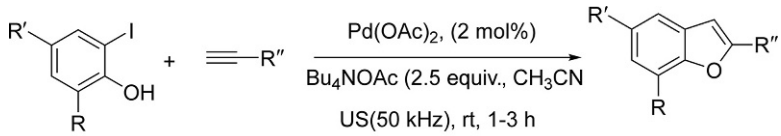
ultrasonic irradiation (Table 9). They were successful to synthesize 18 numbers of 2-arylindole derivatives using their reaction protocol at ambient temperature (30°C) in CH_3CN as solvent in the absence of ligand, copper, and amine bases. They later

Table 9 Yield comparison at different times for Scheme 7 ($R_1 = CH_3$, $R_2 = Ts$, $R_3 = Ph$).

Stirring at room temperature	Time (h) Yield (%)[a]	5 39	12 48	18 58	24 64	30 71	36 71
Ultrasonic irradiation	Time (h) Yield (%)[a]	3 58	3 65	45 74	6 74		

[a]Isolated yields.
Credit: S.S. Palimkar, P. Harish Kumar, R.J. Lahoti, K. V. Srinivasan, Ligand-, copper-, and amine-free one-pot synthesis of 2-substituted indoles via Sonogashira coupling 5-*endo*-dig cyclization, Tetrahedron. 62 (2006) 5110.

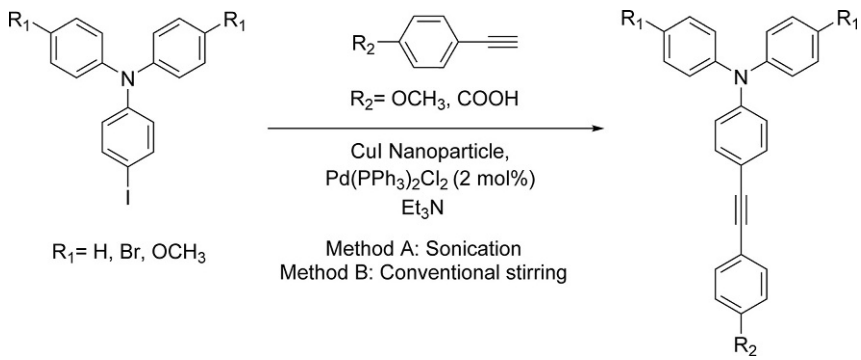
extended their methodology for the synthesis of benzo[*b*]furans/nitro benzo[*b*]furans starting from iodophenols and terminal alkynes under identical condition (Scheme 8) [44]. In situ formation of Pd(0) nanoparticles was confirmed by TEM analysis while the role of ultrasonication in promoting the reaction was substantiated by control experiments.



R = H, I, OMe, CHO
R' = H,CHO, NO_2, I, Cl, Me
R"= Ph, p-tolyl, 4-methoxyphenyl, 3-fluoro phenyl, methanol, 1-ethanol, 2-propan-2-ol

Scheme 8 Synthesis of 2-substituted benzo[*b*]furan under ultrasonic irradiation. *Credit: S.S. Palimkar, V.S. More, K.V. Srinivasan, Ultrasound promoted copper-, ligand- and amine-free synthesis of benzo[b]furans/nitro benzo[b]furans via Sonogashira coupling-5-*endo-dig*-cyclization, Ultrason. Sonochem. 15 (2008) 855.*

Recently, Safaei-Ghomi et al. reported sonochemical synthesis of five numbers of arylethynyl linked triarylamines from iodophenyl diaryl amines and substituted phenyl acetylenes via Sonogashira cross-coupling using $Pd(PPh_3)_2Cl_2$ as catalyst and CuI nanoparticle as cocatalyst in solvent-free condition (Scheme 9) [45]. They carried out the synthesis under both silent condition and ultrasonic irradiation and found the later significantly advantageous than the former which is evident from Table 10. Better efficiency of the methodology under ultrasonic irradiation was attributed to better adsorption on the catalyst surface as well as higher mass transport of organic compounds among the liquid phase and the catalyst surface. Authors assumed that dispersed CuI nanoparticles in the solution afforded additional nucleation sites for cavity formation over its surface during sonication which facilitated the reaction.



Scheme 9 Synthesis of arylethynyl linked triarylamines by Sonogashira coupling. *Credit: J. Safaei-Ghomi, Z. Akbarzadeh, Sonochemically synthesis of arylethynyl linked triarylamines catalyzed by CuI nanoparticles: a rapid and green procedure for Sonogashira coupling, Ultrason. Sonochem. 22 (2015) 368.*

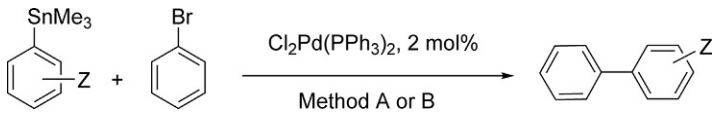
Table 10 Synthesis of arylethynyl linked triarylamines via Scheme 9 under thermal heating (method A) and sonication (method B).

			Method A[a]		Method B[b]	
Entry	**R_1**	**R_2**	**Time (min)**	**Yield (%)[c]**	**Time (min)**	**Yield[b](%)[c]**
1	H	H	360	47	30	75
2	4-Br	H	400	39	45	65
3	4-OCH_3	H	300	51	30	79
4	H	4-OCH_3	300	58	30	88
5	H	4-COOH	360	49	45	76

[a]Reaction condition: iodo phenyl diarylamine (1 mmol), arylacetylne (1 mmol), $Pd(PPh_3)_2Cl_2$ (2.5 mol%), CuI nanoparticle (2.5 mol%) and Et_3N (5 mL), stirring at 50°C.
[b]Reaction condition: iodo phenyl diarylamine (1 mmol), arylacetylne (1 mmol), $Pd(PPh_3)_2Cl_2$ (2.5 mol%), CuI nanoparticle (2.5 mol%) and Et_3N (5 mL), sonication (20 kHz, 50 W).
[c]Isolated yields.
Credit: J. Safaei-Ghomi, Z. Akbarzadeh, Sonochemically synthesis of arylethynyl linked triarylamines catalyzed by CuI nanoparticles: a rapid and green procedure for Sonogashira coupling, Ultrason. Sonochem. 22 (2015) 369.

Sonochemical Stille coupling

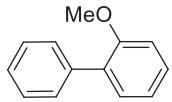
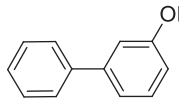
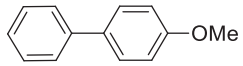
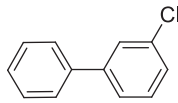
Concept of using ultrasonic irradiation in Stille coupling is not too old, the first report being published by Domini et al. in 2012 only [46]. They demonstrated synthesis of unsymmetrically substituted biphenyls via a sonochemical variation of the Stille coupling (Scheme 10) and the results were compared with the conventional silent reaction (Table 11). They concluded that sonication significantly enhances the usefulness of the methodology by resulting products in higher yield within a shorter time period. They



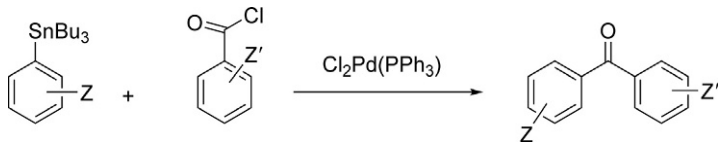
Scheme 10 Cross-coupling reactions of aryl stannanes and bromobenzene. *Credit: C.E. Domini, G.F. Silbestri, B. Fernández Band, A.B. Chopa, Ultrasound-assisted synthesis of unsymmetrical biaryls by Stille cross-coupling reactions, Ultrason. Sonochem. 19 (2012) 412.*

carried out comparison of the reactivity of trimethyl versus tributylstannanes with bromobenzene and observed that the former reacts more effectively than the later. In the following year, they reported synthesis of benzophenones by Stille cross-coupling reactions of aryl stannanes with aroyl chlorides under identical condition (Scheme 11) [47]. Here too, they made comparison of their methodology under thermal as well as ultrasonic irradiation and found that ultrasonic irradiation results in significant improvement in product yield as well as reaction time (Table 12).

Table 11 Comparison of product yields via Scheme 10 under thermal heating (method A) and sonication (method B).

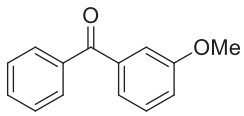
Entry	*Z*	Product	Method A[a] (conventional heating) Yield (%)[b] (20 h)	Method B[c] (Ultrasonication) Yield (%)[b] (30 min)
1	*o*-OMe		73	76
2	*m*-OMe		87	87
3	*p*-OMe		75	97
4	*m*-Cl		65	72

[a]Reaction condition: Bromobenzene (1.2 mmol), arylstannane (1 mmol), $PdCl_2(PPh_3)$ (2 mol%), 80°C, DMF (20 mL).
[b]Quantified by GC, using the external standard method.
[c]Reaction condition: Bromobenzene (1.2 mmol), arylstannane (1 mmol), $PdCl_2(PPh_3)$ (2 mol%), 90°C, DMF (13 mL), US (20 kHz, 600 W).
Credit: C.E. Domini, G.F. Silbestri, B. Fernández Band, A.B. Chopa, Ultrasound-assisted synthesis of unsymmetrical biaryls by Stille cross-coupling reactions, Ultrason. Sonochem. 19 (2012) 412.



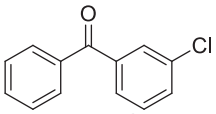
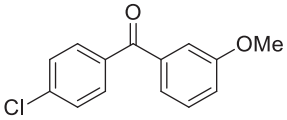
Scheme 11 Cross-coupling reactions of aroyl stannanes and aroyl chlorides. *Credit: M. Luong, C.E. Domini, G.F. Silbestri, A.B. Chopa, Ultrasound-assisted synthesis of benzophenones by Stille cross-coupling reactions. Optimization via experimental design, J. Organomet. Chem. 723 (2013) 46.*

Table 12 Comparison of product yields for Scheme 11 under ultrasonic[a] and silent condition.[b]

Entry	$ArSnBu_3$ (*Z*)	Ar′COCl (*Z*′)	Product	Ultrasonic method[c]	Thermal method[c] 30 min	Thermal method[c] 20 h
1	*m*-OMe	Ph-		96	27	47

Continued

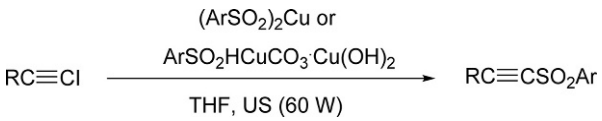
Table 12 Comparison of product yields for under ultrasonic and silent condition—cont'd

Entry	$ArSnBu_3$ (Z)	Ar′COCl (Z′)	Product	Ultrasonic method	Thermal method	
					30 min	20 h
2	*m*-Cl	Ph-		66	20	32
3	*m*-OMe	*p*-ClPh-		59	13	29

[a]Reaction condition: $ArSnBu_3$: PhCOCl (1:1.2), Toluene, 2 mol% of $Cl_2Pd(PPh_3)_2$ with respect to arylsannane, 90°C, ultrasound (20 kHz), 30 min.
[b]Reaction condition: $ArSnBu_3$:PhCOCl (1:1.2), Toluene, 2 mol% of $Cl_2Pd(PPh_3)_2$ with respect to arylsannane, stirring at 90°C for the required time period.
[c]Quantified by GLC, using the external standard method.
Credit: M. Luong, C.E. Domini, G.F. Silbestri, A.B. Chopa, Ultrasound-assisted synthesis of benzophenones by Stille cross-coupling reactions. Optimization via experimental design, J. Organomet. Chem. 723 (2013) 47.

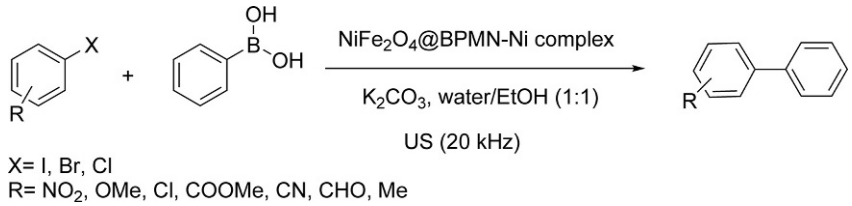
2.1.4 Sonochemical C—C coupling in the presence of metal species other than Pd

An early example of sonochemical C—C coupling was reported by Suzuki et al. in which they carried out straightforward synthesis of alkynyl sulfones starting from alkynyl halides and copper sulfonates in THF under sonication [48]. They showed that the synthesis could be carried out by ultrasonic irradiation of aryl sufonic acid and alkynyl halides in the presence of commercial basic copper carbonate where in situ generated copper sulfonates underwent C—C coupling with alkynyl halides in a tandem process (Scheme 12). Recently in 2018, Naeimi et al. reported magnetically recyclable bis(propyl malononitrile) Ni(0) complex nanocatalyst catalyzed sonochemical Suzuki coupling for green and efficient synthesis of biphenyl derivatives (Scheme 13) [49].

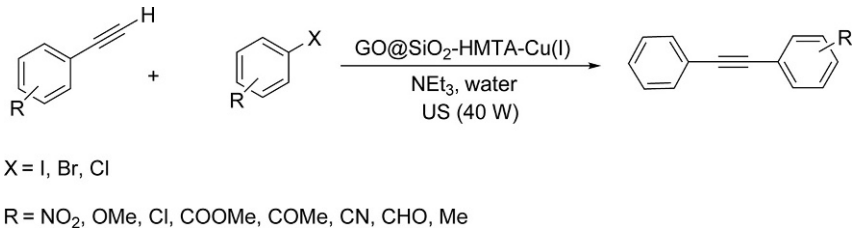


Scheme 12 Sonochemical synthesis of alkynyl sulfones. *Credit: H. Suzuki, H. Abe, A new straightforward synthesis of slkynyl sulfones via the sonochemical coupling between alkynyl halides and copper sulfinates, Tetrahedron Lett. 37 (1996) 3718.*

The same research group in the same year reported Pd-free sonochemical protocol for Sonogashira cross-coupling reaction in the presence of hexamethylenetetramine copper diiodide immobolized on graphene oxide nanocomposite as catalyst in water (Scheme 14) [50].



Scheme 13 Suzuki cross-coupling using $NiFe_2O_4$@BPMN-Ni complex under ultrasonic irradiation. *Credit: F. Kiani, H. Naeimi, Ultrasonic accelerated coupling reaction using magnetically recyclable bis (propyl molononitril) Ni complex nanocatalyst: a novel, green and efficient synthesis of biphenyl derivatives, Ultrason. Sonochem. 48 (2018) 272.*

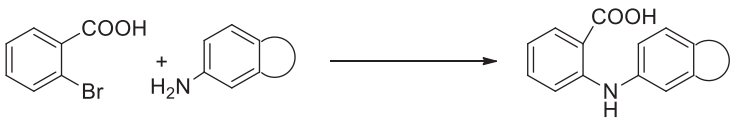


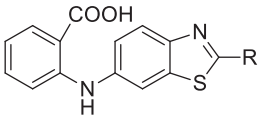
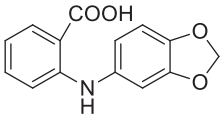
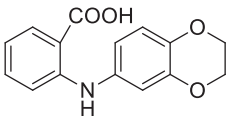
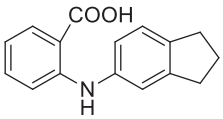
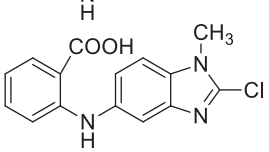
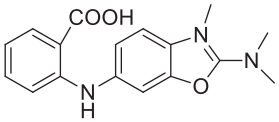
Scheme 14 Sonogashira cross-coupling of aryl halides and phenyl acetylenes in the presence of GO@SiO_2-HMTA-Cu(I) under ultrasonic irradiation. *Credit: H. Naeimi, F. Kiani, Hexamethylenetetramine copper diiodide immobilized on graphene oxide nanocomposite as recyclable catalyst for sonochemical green synthesis of diarylethynes, ChemistrySelect 3 (2018) 13316.*

2.2 Sonochemical protocol in C—N coupling reactions

In comparison to C—C coupling reaction, C—N coupling reactions have been less exposed to ultrasonic irradiation. Robin et al. reported the synthesis of *N*-aryl anthranilic acid derivatives bearing dioxolo, dioxino, cyclopent, and imidazole supplementary ring systems by ultrasonic Ulmann condensation reaction in butan-2-one in the presence of Cu—Zn metal couple [51]. They compared their results with the reported results under silent reaction condition which are summarized in Table 13. From the table, it is very clear that ultrasonic irradiation could improve the Ulmann-Goldberg condensation reaction in yield and reaction time.

Table 13 Comparison of conventional heating and ultrasonic irradiation in Ulmann-Goldberg condensation reaction.

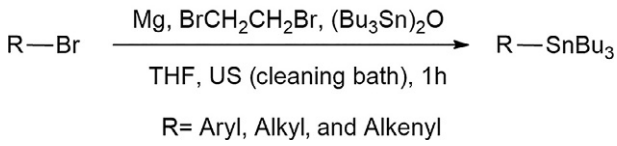


Structure	Product yield Conventional heating (source)	Product yield Ultrasonic irradiation[a]
	R = Cl, 25%, 12 h R = H, 24%, 12 h R = CH_3, 23%, 12 h (*Tetrahedron Lett.* **34**, 2609, 1993)	86%, 3 h 72%, 3 h 81%, 3 h
	21%, 6 h (*J. Heterocyclic Chem.* **29**, 73, 1992) 42%, 12 h (*Magn. Reson. Chem.* **35**, 556, 1997)	45%, 3 h
	58%, 3 h (*J. Heterocyclic Chem.* **30**, 1101, 1993) 53%, 12 h (*Magn. Reson. Chem.* **35**, 556, 1997)	81%, 3 h
	33%, 12 h (*J. Chem. Research* **4**, 115, 1998)	70%,3 h
	51%, 3 h (*J. Heterocyclic Chem.* **34**, 1781, 1997)	87%, 3 h
	Never done	90%, 3 h

[a]Reaction condition: Amino heterocycle (10 mmol), *o*-bromobenzoic acid (11 mmol), and K_2CO_3 (12 mmol), Cu/Zn (0.06 g), butan-2-one (25 mL), ultrasonic irradiation (35 kHz), 80°.
Credit: M. Robin, V. Pique, R. Faure, J.P. Galy, Ultrasonic irradiation of the Ullmann condensation: application to the preparation of dioxolo, dioxino, cyclopent, and imidazolo anthranilic acid derivatives, J. Heterocycl. Chem. 39 (2002) 1083.

2.3 Sonochemical protocol in C—Sn coupling reactions

A facile and efficient synthetic methodology for organostannanes via sonochemical Barbier reaction has been found reported by Lee et al. (Scheme 15) [52]. They investigated and remarked that Mg underwent reaction with 1,2-dibromoethane to generate $MgBr_2$ in situ which facilitated the organostannane formation. Aryl-, alkyl-, and alkenyl stannanes could be synthesized using the procedure and synthesis of aryl stannanes were found chemoselective for aryl bromide.



Scheme 15 Sonochemical synthesis of organostannanes. *Credit: A.S.Y. Lee, W.C. Dai, A facile and highly efficient sonochemical synthesis of organostannane via Barbier reaction, Tetrahedron 53 (1997) 860.*

3 Concluding remark

In conclusion, sonication has been successfully used for various organic coupling reactions. Most of the reports made comparison of the developed sonochemical methodologies with corresponding silent conventional methodologies and found that the sonochemical methodologies are superior to conventional methodologies in terms of percentage of conversion, product yield, and reaction time. Only a few methodologies have been seen to focus on studying the effect of sound waves on reaction mechanisms. Relative to C—C coupling reactions, C—X (X is an element other than C and H) coupling reactions have been less studied under ultrasonic irradiation. So, it is felt that there is enough scope to develop sonochemical methodologies for C-X coupling reactions and new sonochemical protocol for C—C coupling reactions. Such methodologies, which are greener than their conventional counterpart will be valued additions to the existing coupling procedures.

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CHAPTER 8

Sonochemical protocol for protection and deprotection of functional groups in organic synthesis

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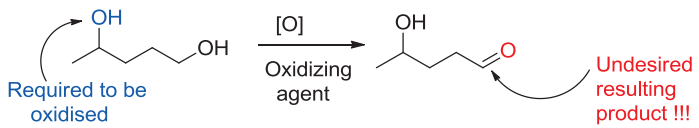
1. Introduction

The protection and deprotection of functional groups in synthetic organic chemistry with high chemoselectivity and efficiency, is always a challenging task, due to inhibition of forming undesired bonds as well as other unwanted reactions [1, 2]. Particularly, in multistep reaction with multifunctional groups in organic synthesis face sequential protection/deprotection to get the desired molecules. In that respect, the reactive sites of a compound having multiple functional groups are in general temporarily blocked to carry out the reaction at one particular reaction center, and it can be brought off by appropriate protection and deprotection of functionality to survive in the chemical environments. Keeping in mind, the orthogonal protection protocols are selected mildly so that expected demasking could be focused by alternative cleavage mechanisms rather than the rate of reactions. A simple example is displayed below to provide the answer to the question: why protecting and deprotecting of the functional group is important and how it is carried out? When 1° and 2° alcohol groups are present simultaneously in the molecule, oxidation of the 2° alcohol group could be accomplished with the assistance of oxidizing agents like PCC or DCC, but the primary alcohol is more sensitive (reactive) to oxidation (Scheme 1) than the others.



Scheme 1 Oxidation of alcohol group and selectivity.

Thus, to solve the problem, two additional steps are required; firstly, the protecting group could be introduced to protect primary alcohol and makes it inert toward oxidation and facilitating the secondary hydroxyl group oxidation easily to get the intermediate keto derivative. After successful oxidation, the cleavage of the protecting group also

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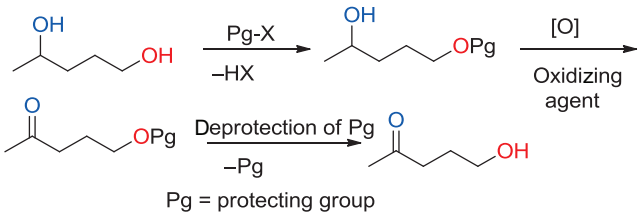
could be performed straightforwardly regenerating the primary alcohol easily, as shown in Scheme 2.



Scheme 2 Oxidation of the hydroxy group and selectivity using protecting groups.

This context indicates that the functional groups which are required to be preserved, protected by proper functionality and then the required reactions are implemented on the desired functional group, keeping the other functionalities intact during the reaction period/workup and in purification steps. After completion of the reaction, the parent functional group could be restored by cleaving protecting group, which is presented graphically in Fig. 1. Therefore, a desirable synthetic scheme cannot be suitable if the corresponding protecting groups present in the molecule are not properly chosen. Perhaps, Emil Fischer has first recognized the necessity to temporally block a functional group for permitting regioselective bond formation in carbohydrate synthesis [3]. The literature report finds that Bergmann and Zervas developed the first "modern" protecting group benzyloxy carbonyl (Z) [4] in 1932.

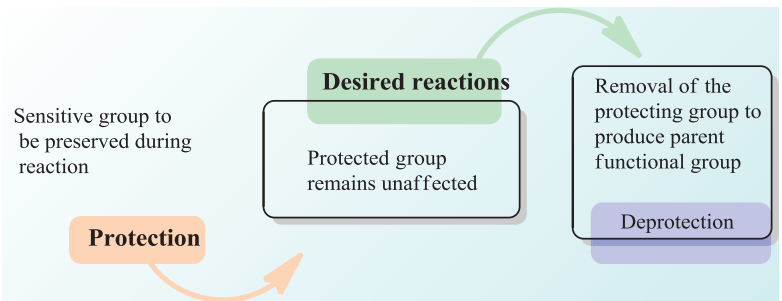


Fig. 1 Protection and deprotection sequence in chemical reactions.

2. Different energy source for chemical reaction

Since chemical reactions come off through making and breaking of bonds, henceforth for any protection/deprotection of functional groups necessitate an energy source to activate molecules and cleave/form bonds. The main focus in chemical modification of a functional group in a molecule is its selectivity (kinetic/chemoselectivity) in the presence of other reacting groups with notable yields. In that respect, an effective way for the

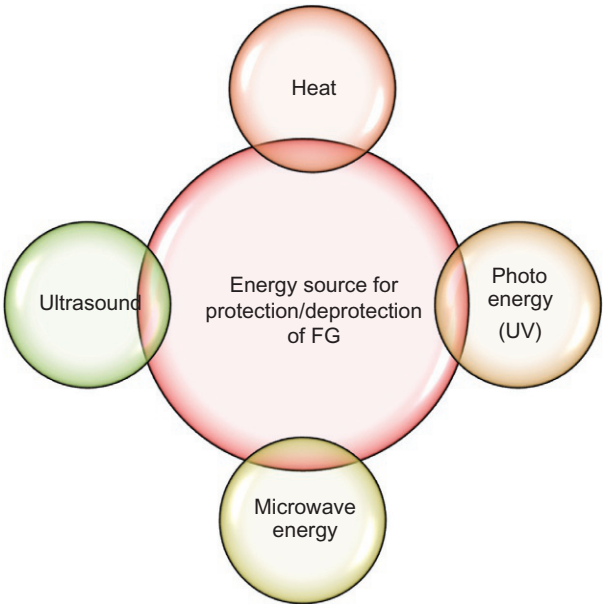


Fig. 2 Energy sources used for protection/deprotection reactions of functional groups.

protection and cleavage of functionality is highly indispensable to synthesize complex molecules. Not only the fulfilling of the economic criteria but also it should be a time saver and environmentally friendly. As a consequence, besides the proper synthetic procedures and reagents, the energy source (Fig. 2) is also vital in the active chemical process.

Thermal conditions are simple and classical mode for chemical synthesis, as easily accessible in a laboratory friendly environment unless otherwise, the reactions are extremely high pressure/temperature-dependent. Nonetheless, in the sensitive molecule, like biomolecules peptides/DNA, which is denatured during heating at a higher temperature, low-temperature maintenance is necessary. In maintaining an atom economy in green chemical reactions, the reactions are always designed to produce the highest yield with a minimum number of steps and also using less energetic approaches. The novelty is the improvement of environmentally sound techniques in their chemistry that could address many inevitable challenges, in working with chemical reactions, and in the quality and quantity of the products by developing greener reactions.

On top of that, the synthetic scheme should be designed to crop the molecules which are nontoxic to human as well as the environment. Nowadays, the attention is toward the green approaches that have the potential to the escalation of yields of desired products, minimization of time and by-products, and simplification the operations in chemical production by using nontoxic, less hazardous, and less carcinogenic nonvolatile organic solvents [5]. Though natural energy source, photochemical energy is used in few cases [6], it is limited, and also UV-light used for this purpose is not always safe [7].

In this regards, ultrasound energy is emerging among various environmentally friendly energy sources for chemical reactions which lead to low energy requirements, low waste, high efficiency, and reaction rate enhancement by many orders of magnitude [8, 9]. Although chemical reactions are also performed under microwave irradiation as green energy well in chemical reactions to protect and deprotect functional groups rapidly, it is limited as high boiling solvents are required and temperature control is difficult. Sonochemistry is evolving as an advanced field in the organic synthesis because of its benefits like shortening reaction steps, effective reactions of sterically hindered groups, and less harsh circumstances like low temperature, solvent-free as well as additives free reactions [10]. Recently, it is broadly applied as an energy source to make radicals and initiate the electron transfer process in chemical reactions [11]. Time and economically bonafide approaches to form and remove the protected compounds are desirable for the synthesis of complex molecules. Ultrasound promotes an unusual mechanism for the provision of high energy-assisted chemistry. It can reduce the reaction time significantly; improve the reactivity of the reactant, resulting in superior yield with excellent stereoselectivity. The remarkable acoustic cavitation makes sonochemistry a unique tool for the excellent behavior for chemical reactions. Usually, in the process of ultrasound-mediated organic reactions, the range of ultrasound energy is within the range of 20 kHz–1 MHz [12], and for protection and deprotection reactions, the frequency is ~20–50 kHz (Fig. 3).

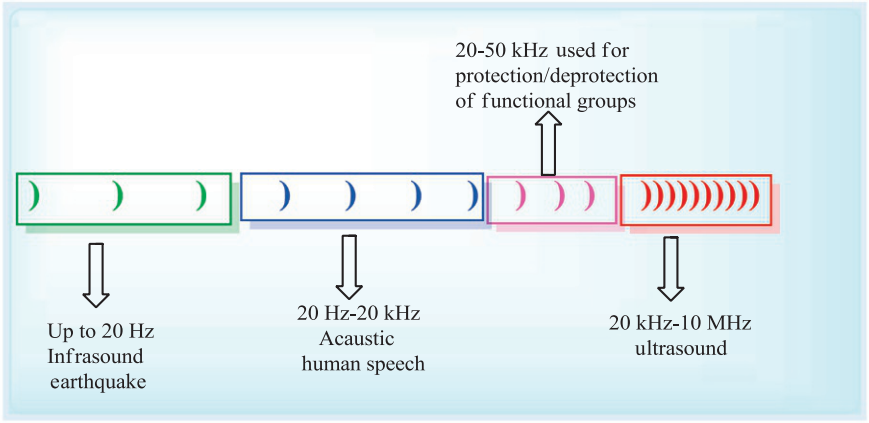


Fig. 3 Range of ultrasound waves and its use.

3. Mechanisms for the generation of energy in sonication

In 1927, Loomis, first applied ultrasound (100–500 kHz) energy for the iodine "clock" reaction [13]. Outstanding progress in the area of sonication-assisted organic reactions has been noticed, particularly for their superior yields, better stereoselectivity, a lesser reaction times, increased reactivity of reactant/reagents/catalysts, switching of the reaction pathway, avoidance of phase-transfer catalysts, activation of metals and solids, improved nanoparticle synthesis, and initiation of radical polymerization.

In recent times, this green technology is a highly encouraging energy source to execute chemical reactions, rather than the classical one, wherein the reactions proceed via an interesting cavitation phenomenon, producing energy enough to alter rotational and vibrational molecular states. This ultrasound-mediated organic synthesis is directed by parameters like amplitude and frequency of the applied sound field, surface tension, temperature, vapor pressure, vessel and probe geometry, etc. Interestingly, the creation of acoustic cavitations of microbubbles that grow and collapse incessantly, reaching temperatures of 5000–8000 K and pressures > 10,000 atm on a nanosecond timescale within the vapor phase of the bubble, subsequently swift cooling at a rate as fast as 10^9 K/s (Fig. 4) [14].

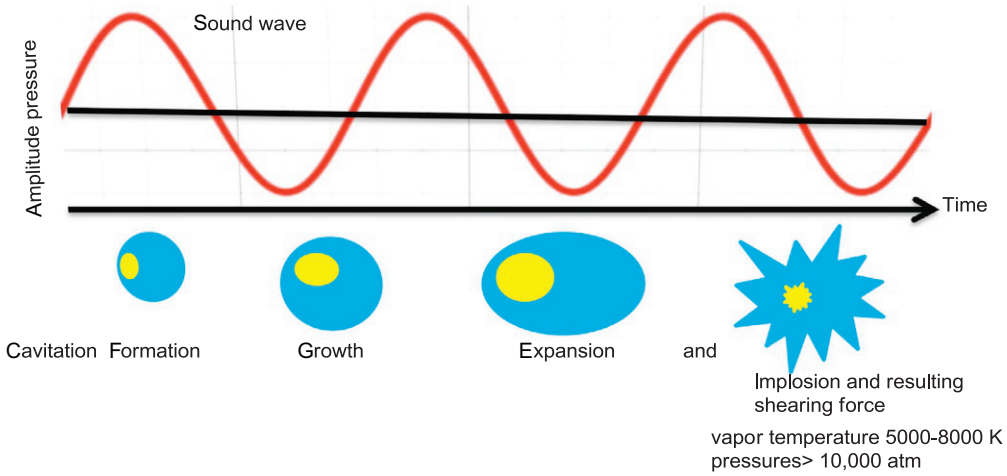


Fig. 4 Acoustic cavitation for the generation of energy in sonication.

Surprisingly, the sonication mediated reactions are independent of acidity, basicity, or dipole moment. The inadequate yields acquired from classical ways and requirement of expensive catalysts and limited scope of substrates, this ultrasound irradiation has occurred in the literature as a beneficial approach in synthetic chemistry predominantly, to promote environmentally friendly protocols for the protection and removal of different functional groups such as amine, hydroxy, carboxyl, carbonyl, amide, and so on.

4. Brief discussion on protection and deprotection of functional groups

The well-known and sensitive functional groups in synthetic organic chemistry are a hydroxy group of alcohol/phenol, the carbonyl group of aldehyde/ketone, amine, carboxylic acid group, and so forth. Henceforth their role in modern chemical reactions is always demanding. Appropriate protecting groups are required for these functional groups, as nature and chemical reactivity is distinguishable for unlike functional groups (Fig. 5). The regeneration of parent functional groups through selective deprotection applying suitable condition is always thought provoking.

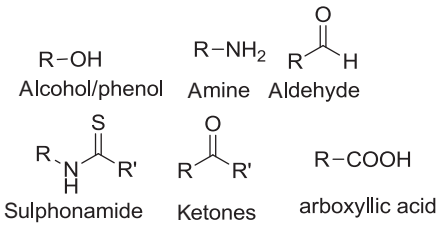


Fig. 5 Few common functional groups.

4.1 Protecting groups for hydroxy

Firstly, we deliberate about the hydroxy functionality as this is present in numerous molecules, particularly, the most abundant carbohydrates, polysaccharides, hydroxy acids, polyhydroxylated open-chain compound, etc. The wide ranges of the hydroxy group present in organic molecule make it key to protect as it is quite sensitive to oxidation and reduction. The main category of protection of hydroxy is the esterification, etherification, and ether silyl protection. The protection of the hydroxy group with functionality like TBS, TBDPS, MOM, MEM ether, acetate, etc. as shown in Fig. 6 has placed a significant role in organic synthesis.

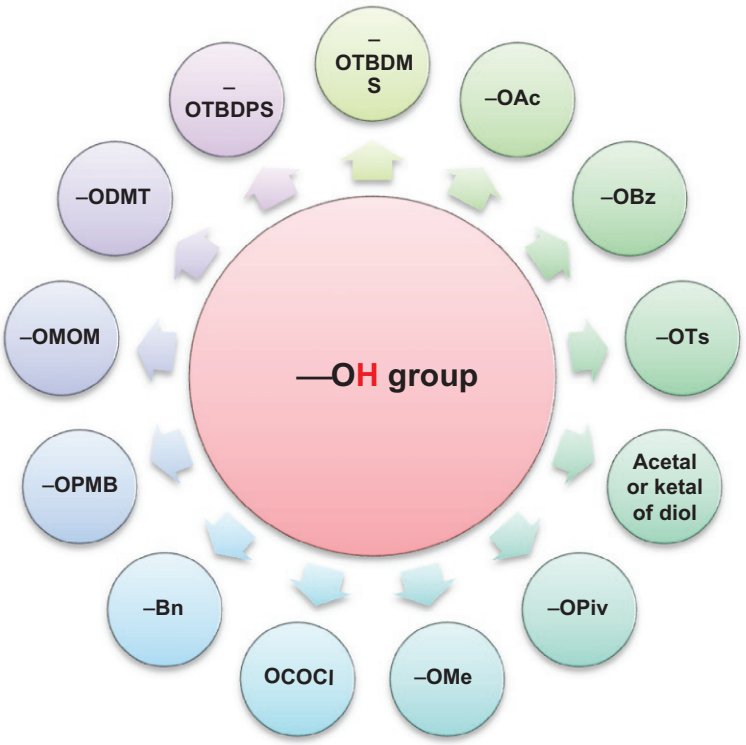
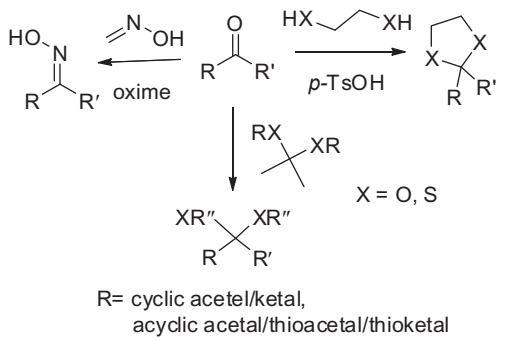


Fig. 6 Different protecting groups for hydroxy.

4.2 Protecting groups for aldehydes and ketones

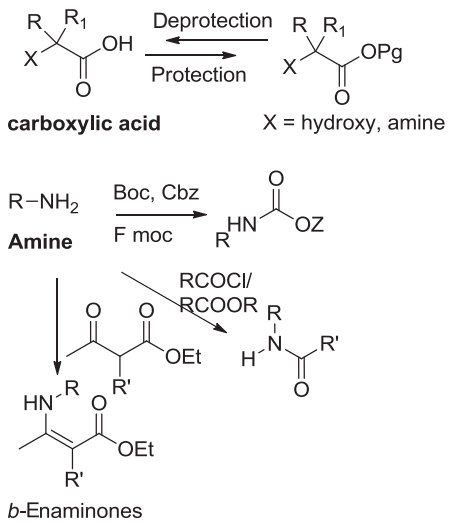
The availability of blocking agents for carbonyl groups in organic synthesis are acetal/ketal, oxime, and thioacetal/thioketal as represented in Scheme 3.



Scheme 3 General protecting groups for carbonyls.

4.3 Protecting groups carboxylic acids/amines

Carboxylic acid functionality is part of the amino acids/hydroxy acid/and required to be protected during peptide synthesis as well as various chemical transformations. Protection of the carboxylic acid conducted as ester, amide, and anhydride, etc. are regenerated after other functional group manipulation under acidic/basic hydrolysis to their corresponding parent functional group. Amino acids are essential to the formation of protein building blocks, and it is required to be protected and deprotected during peptide synthesis in addition to other aliphatic and aromatic amines should also be preserved during chemical reactions. Some relevant protecting groups for amine are alkyl, acetyl, Boc, Fmoc, β-enaminones, etc. (Scheme 4).



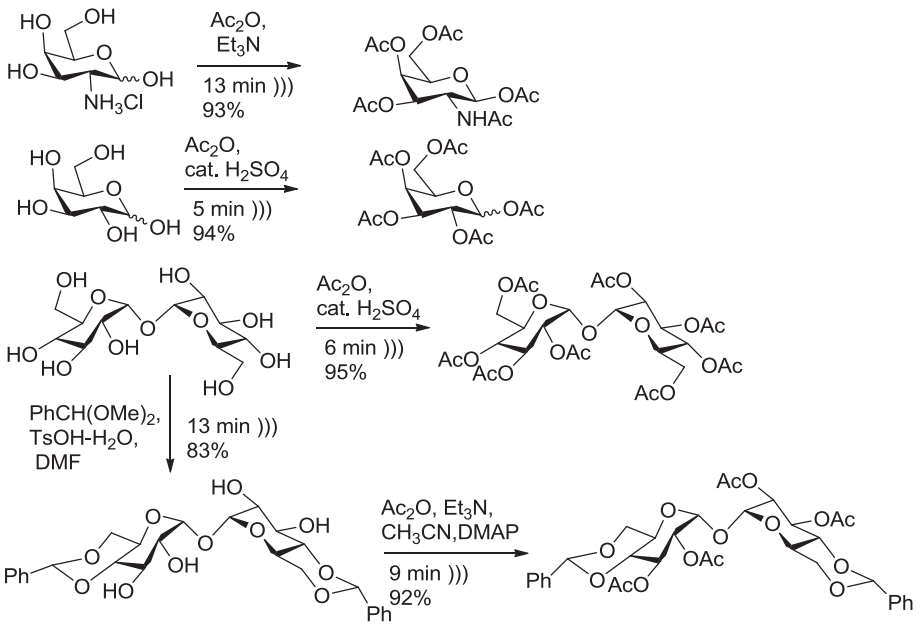
Scheme 4 Protecting groups for a carboxylic acid group and protection/deprotection.

5. Ultrasound-promoted protection and deprotection of hydroxy group (—OH) in carbohydrates

Carbohydrates or polysaccharides which contain multiple hydroxy groups play a vital role in organic chemistry as it is a significant part of biomolecules and associated with both sources of the precursors of organic reactions as well as derivatives like nitrocellulose, rayon, etc. These polyhydroxylated molecules required protection and deprotection of the hydroxy group and these procedures are well documented in the literature [15]. These procedures were time-consuming, and the use of ultrasound in these reactions reduced the time for reactions significantly. Herein, firstly we will discuss the monosaccharides, which in particular are useful chiral pools as a starting material to endeavor natural products and pharmaceutically active ingredients synthesis [14]. The beneficial effect of sonochemical reactions emerging in the literature assists in taking advantage to apply this energy source in the area of carbohydrate chemistry [16].

5.1 Acetylation and ketal protection

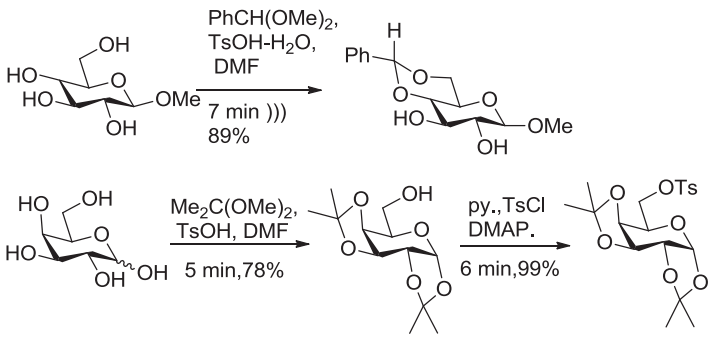
The blocking and removal of hydroxy functionalities in carbohydrates with acetyl, benzylidene, isopropylidene, pivaloyl, or benzyl groups, as well as the migration of these groups, are a common subject [17–21]. In 2006, Chang et al. have



Scheme 5 Acetylation of hydroxy functionality of monosaccharides under sonication.

established that for synthesis and functionalization of carbohydrates and particularly protection and deprotection as well as protecting group migration may be better executed under ultrasound irradiation with superior results concerning yields and reaction times [22, 23]. The hydroxy groups present in a different position in monosaccharide and disaccharides were acetylated within 5–15 min and with 83%–95% yields, as shown in Scheme 5. With the help of sonication, the acetylation of all the four hydroxy groups of galactose has achieved in only 5 min. The experiment discloses that glucosamine takes 13 min for acetylation of all four hydroxy groups under sonication reaction.

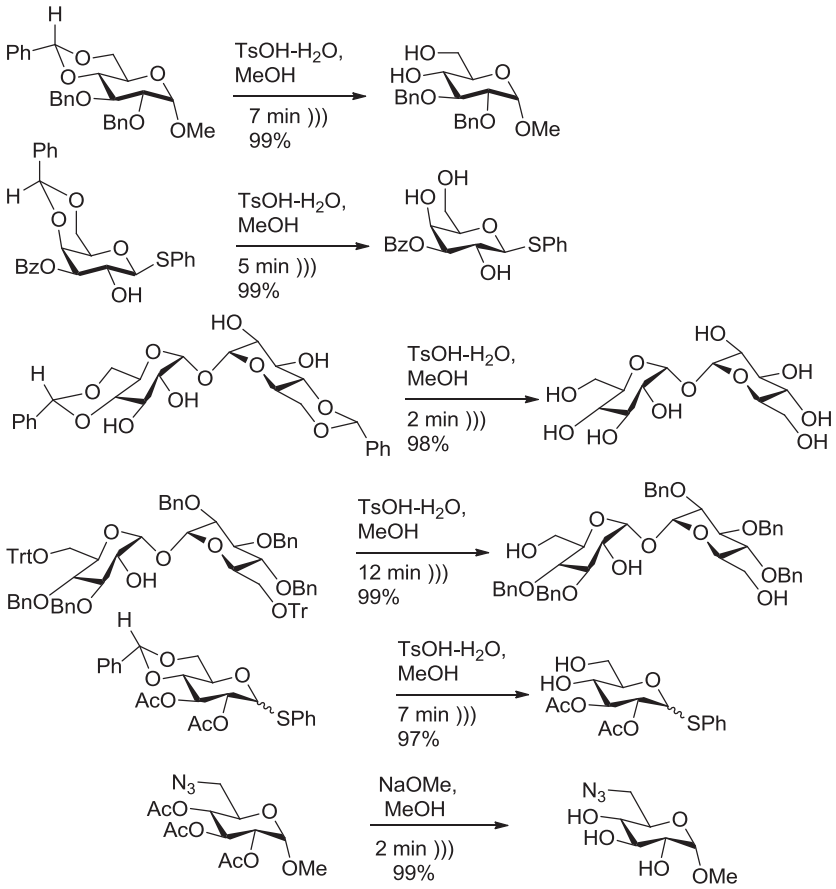
Protection of hydroxy group in carbohydrates (hydroxy groups in 1,2-relationships) is best performed with acetyl and ketal group which takes hours by the conventional method. Sterically hindered disaccharides like trehalose can also be protected by ketal and acetal group in much shorter reaction time with high yield sonochemically. Tosylation has functioned very nicely under microwave irradiation, too (Scheme 6) [23].



Scheme 6 Ketal protection of 1,2-hydroxy groups.

5.2 Deprotection of acetate, trityl, and benzylidene functionalities

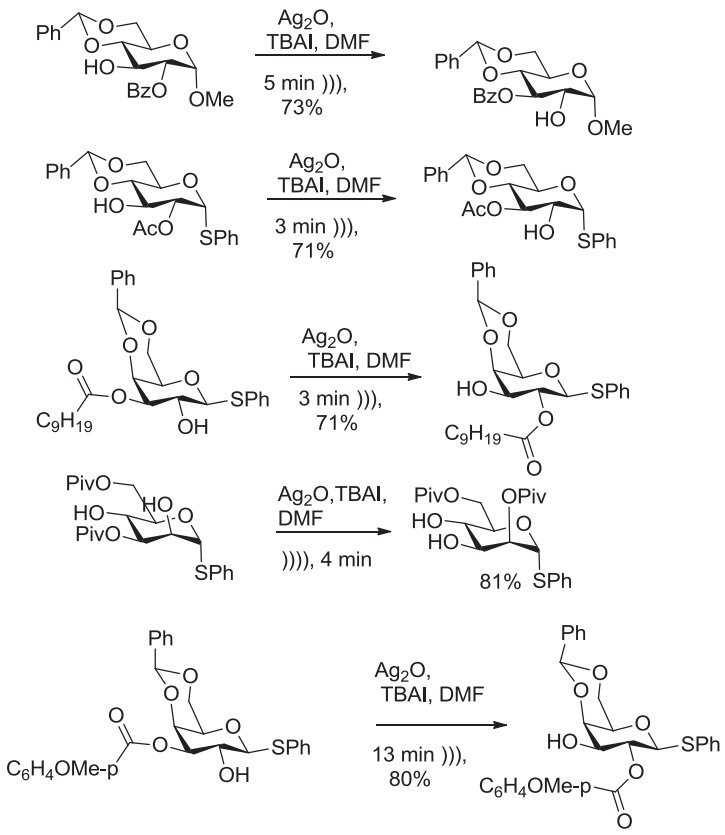
The experimental results to cleave acetyl and benzylidene groups under sonication within a few minutes providing the corresponding deprotected product in good yields are depicted herein. The trityl group was also deprotected smoothly and successfully in nearly 12 min and quantitative yield, which generally demands harsher conditions in conventionally owing to steric hindrance (Scheme 7). Furthermore, the ketal group was also demasked within 2–7 min under sonication.



Scheme 7 Deprotection of acetate, trityl, and benzylidene functionalities.

5.3 Migration of functional groups

Normally, migration of acyl group within the carbohydrate scaffold ensures hours or even days to complete the reaction [23]. In comparison, it can be over within much less time by ultrasound assistance (Scheme 8). In the presence of the mild base silver oxide and TBAI, the migration of the benzoyl, acetyl, and pivaloyl esters functionality under sonication manufactured the desired compounds in 3–13 min and 71%–80% yield. For altering the position of protecting groups, a solution of starting compound (0.12 mmol), silver oxide (0.12 mmol), and tetrabutylammonium iodide (TBAI) (0.012 mmol), in anhydrous DMF (5 mL) was sonicated at room temperature [24].



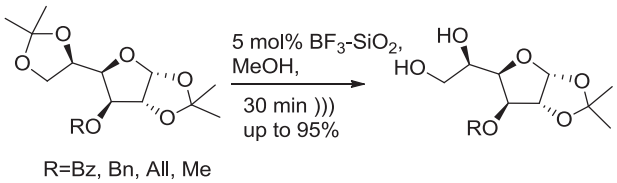
Scheme 8 Migration of hydroxy, protected functional groups.

5.4 Ultrasound-assisted selective deprotection of terminal acetonides

Extensively used functional groups to protect both terminal and internal 1,2- and 1,3-diols in nucleoside and carbohydrate chemistry is simple isopropylidene group. A variety of catalysts employed for the deprotection of terminal acetonides, including protonic acids such as HCl, HBr, HOAc, H_2SO_4, and TFA. Lewis acid-based reagents such as $CeCl_3.7H_2O(COOH)_2$, $(Zn(NO_3)_2{\cdot}6H_2O$, $BiCl_3$, VCl_3, $In(OTf)_3$, and $La(NO_3)_3$, are also employed for this program. Most of these processes suffer from disadvantages such as strong acidic medium, expensive metals, longer reaction times, and high reaction temperatures [25]. In other cases like protonic acids or Lewis acid-based reagents in homogeneous solutions, the removal of these catalysts is problematic. Alternatively, use of supported reagents including $FeCl_3{\cdot}6H_2O$ on silica H_2SO_4 on silica, $HClO_4$ on silica, and $NaHSO_4$ on silica have solved work up the problem by easy

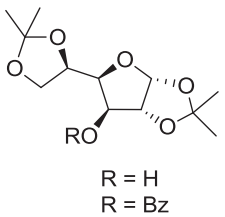
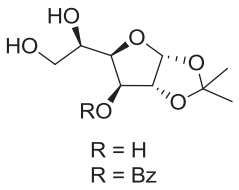
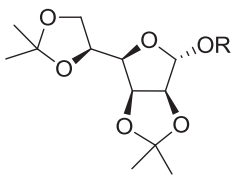
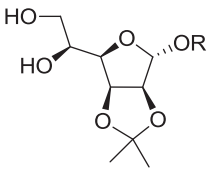
removal but created other drawbacks, including lower yields, long reaction periods, and inharmoniousness with few other protecting groups [26].

Junlong et al. stated a facile and convenient acid-catalyzed selective cleavage of terminal isopropylidene in the presence of ultrasonic irradiation (Scheme 9) [27] (Table 1).



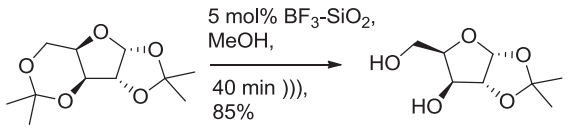
Scheme 9 Selective deprotection of the terminal *O*-isopropylidene with BF_3-SiO_2 under ultrasound.

Table 1 Deprotection of the terminal *O*-isopropylidene in thermal and sonication conditions.

Entry	Substrate	Product	Time (min) Stirring	Yield (%) Stirring	Time (min))))	Yield (%))))
1	 R = H R = Bz	 R = H R = Bz	180 180	78 76	30 30	85 89
2	 R= Bz R=Bn	 R= Bz R=Bn	150 180	82 81	30 30	90 92

To do the removal reaction, methanol (5 mL) containing $BF_3{\cdot}OEt_2$ (4.2 mmol) and preheated silica gel (0.4 g) were stirred for 1 h at r.t. following concentration on a rotary evaporator at 40°C and then drying at r.t. for 2 h to get a solid mixture. To the solution of acetonide protected sugar derivatives (1 mmol) in CH_3OH (10 mL), prepared BF_3-SiO_2 (5 mmol%) was added, and the heterogeneous mixture was shaken in an ultrasonic cleaner at rt. for 150–180 min to afford the product in high yield (85%–92%). Likewise, the

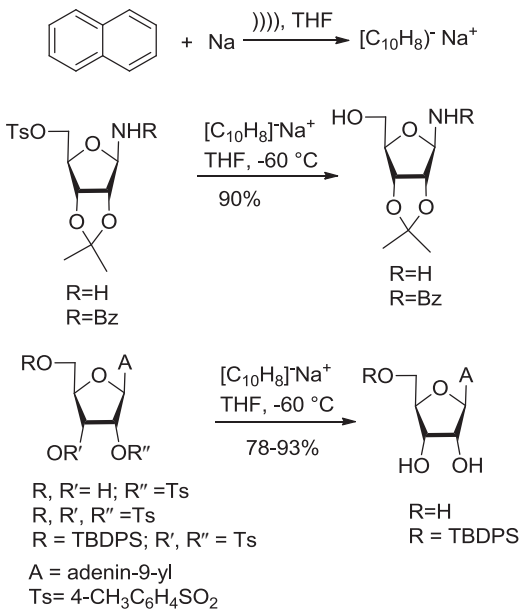
acetonide in D-xylofuranose derivative was deprotected and formed the corresponding diol in a short time (30–40 min) and good yields (Scheme 10). At this point, ultrasound irradiation increases the reaction rate as well as yield and protection to acid-sensitive groups. These solid-supported Lewis acids make easy separation of products too.



Scheme 10 Deprotection of the D-xylofuranose derivative by Lewis acid and sonication.

5.5 Sugar *O*-tosyl groups deprotection from purine nucleosides

The intensive efforts to deblock tosyl functional groups thermally, works successfully with ultrasonic irradiation upon reaction with sodium naphthalenide. The high reduction potential of sodium naphthalenide assists in the removal of 2′-, 3′-, or 5′-*O*-tosyl groups of sugar derivatives through in situ preparation of sodium naphthalenide from sodium and naphthalene in THF under ultrasound irradiation. The successful approach has been devoted to removing tosyl group in 2′,3′-*O*-isopropylidene-5′-*O*-tosyluridine or 2′-*O*-tosyluridine using sodium naphthalide (Scheme 11) at −78°C to furnish 2′,3′-*O*-isopropylideneuridine or uridine, respectively with 80%–90% along with 5%–15% by-products [28].

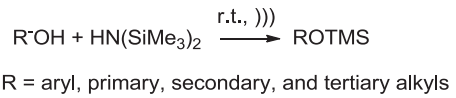


Scheme 11 *O*-Tosyl groups deprotection from purine nucleosides with the help of sonication.

6. Ultrasound-promoted protection and deprotection of hydroxy group (—OH) in noncarbohydrates

6.1 Ultrasound mediated catalyst-free protection of alcohols

The additional and worthy protecting group of hydroxy functionalities is the silyl ether, and their formation is valuable. Among the silyl ethers, though *tert*-butyldimethylsilyl ether is most frequently used protecting group [29], the use of cheap and commercially available reagent is currently increasing [29b, 30–32]. Protection of the hydroxy group is being set out with ultrasound assistance by Mohammad et al. using hexamethyldisilazane (HMDS) to compensate poor silylation power [33]. Protection of varied alcohols and phenols is rapidly performed with hexamethyldisilazane using ultrasound irradiation in the presence of no solvent, or any additive takes place in good yields at room temperature (Scheme 12). Notably, the excellent chemoselectivity was highly visible for competitive protection of hydroxy groups in favor of sterically less hindered alcohols. Ultrasonic irradiation promoted efficient, rapid, solvent-free, and chemoselectively for the synthesis of silyl ethers in the presence of no additive is summarized in Table 2. In the absence of ultrasound irradiation, benzyl alcohol (5.0 mmol) with HMDS (3.0 mmol) mixture under heating in boiling water bath gave only 46% of the same compound after 12 h, but under sonication, reaction completed to the corresponding silyl ether in 10 min (entry 1). Separation of the product was easily worked out after removal of the volatile components and purification through column chromatography. The reaction of other benzylic and aliphatic alcohols, similarly, supplied the desired TMS ethers in 84%–99% yield and in short reaction time (entries 2–8). Protection of secondary alcohols (entry 9–13), tertiary alcohol (entry 14), and phenols (entries 15–16) was also achieved very fast to their respective products under a similar protocol.



Scheme 12 Ultrasound-mediated TMS protection of alcohol.

Table 2 Ultrasound-assisted TMS protection of the hydroxy group.

Entry	Alcohol/phenol	Product (silyl ethers)	Time)))	Yield (%)
1	$C_6H_5CH_2OH$	$C_6H_5CH_2OTMS$	10	99
2	4-$MeOC_6H_4CH_2OH$	4-$MeOC_6H_4CH_2OTMS$	10	99
3	4-$ClC_6H_4CH_2OH$	4-$ClC_6H_4CH_2OTMS$	10	91
4	4-$NO_2C_6H_4CH_2OH$	4-$NO_2C_6H_4CH_2OTMS$	10	84
5	$Ph(CH_2)_3OH$	$Ph(CH_2)_3OTMS$	5	99
6	$PhCH{=}CHCH_2OH$	$PhCH{=}CHCH_2OTMS$	5	99
7	$CH_3(CH_2)_4OH$	$CH_3(CH_2)_4OTMS$	5	98
8	$CH_3(CH_2)_5OH$	$CH_3(CH_2)_5OTMS$	5	99
9	$PhCH(CH_3)OH$	$PhCH(CH_3)OTMS$	20	75

Table 2 Ultrasound-assisted TMS protection of the hydroxy group—cont'd

Entry	Alcohol/phenol	Product (silyl ethers)	Time)))	Yield (%)
10	$CH_3CH_2CH_2CH(CH_3)OH$	$CH_3CH_2CH_2CH(CH_3)OTMS$	20	92
11	Cyclohexyl-OH	Cyclohexyl-OTMS	20	96
12	$CHCCH(CH_3)OH$	$CHCCH(CH_3)OTMS$	20	98
13	$(Ph)_2CHOH$	$(Ph)_2CHOTMS$	20	60
14	$CH_3CH_2C(CH_3)_2OH$	$CH_3CH_2C(CH_3)_2OTMS$	20	75
15	Phenyl-OH	Phenyl-OTMS	20	93
16	2-Naphtyl-OH	2-Naphtyl-OTMS	10	97

Competitive reactions were also designed by the same research group to conquer the chemoselective protection of hydroxy groups, which has briefly discussed in Table 3. These results revealed that aliphatic having less hindered alcohols are more rapidly and selectively react in good to excellent yields (entries 1–3), particularly, protection of primary aliphatic (entry 4) or benzylic alcohols (entries 5–6) dominating over more

Table 3 Ultrasound-assisted solvent-free competitive TMS protection of alcohols.

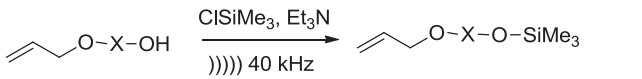
Entry	Alcohol	Product A	Alcohol	Product B	A:B
1	$CH_3(CH_2)_4OH$	$CH_3(CH_2)_4OTMS$	$EtCH_2CH(CH_3)OH$	$EtCH_2CH(CH_3)OTMS$	11.5:1
2	$CH_3(CH_2)_4OH$	$CH_3(CH_2)_4OTMS$	$CH_3CH_2C(CH_3)_2OH$	$EtC(CH_3)_2OTMS$	>99:1
3	$EtCH_2CH(CH_3)OH$	$EtCH_2CH(CH_3)OTMS$	$EtC(CH_3)_2OH$	$EtC(CH_3)_2OTMS$	24:1
4	$CH_3(CH_2)_4OH$	$CH_3(CH_2)_4OTMS$	$C_6H_5CH(CH_3)OH$	$C_6H_5CH(CH_3)OTMS$	13.3:1
5	$CH_3(CH_2)_4OH$	$C_6H_5CH_2OTMS$	$EtCH_2CH(CH_3)OH$	$EtCH_2CH(CH_3)OTMS$	11.5:1
6	$CH_3(CH_2)_4OH$	$C_6H_5CH_2OTMS$	$EtC(CH_3)_2OH$	$EtC(CH_3)_2OTMS$	99:1
7	$CH_3(CH_2)_4OH$	$C_6H_5CH_2OTMS$	$C_6H_5CH(CH_3)OH$	$C_6H_5CH(CH_3)OTMS$	3.5:1
8	$CH_3(CH_2)_4OH$	$CH_3(CH_2)_4OTMS$	$C_6H_5CH_2OH$	$C_6H_5CH_2OTMS$	1.3:1
9	$EtCH_2CH(CH_3)OH$	$H_3CCH_2CH_2CH(CH_3)OTMS$	$C_6H_5CH(CH_3)OH$	$C_6H_5CH(CH_3)OTMS$	1.2:1
10	$EtC(CH_3)_2OH$	$EtC(CH_3)_2OTMS$	$C_6H_5CH(CH_3)OH$	$C_6H_5CH(CH3)OTMS$	1.1:1
11	C_6H_5OH	C_6H_5OTMS	$C_6H_5NH_2$	C_6H_5NHTMS	>99:1
12	HO-4-$C_6H_4NH_2$	TMSO-4-$C_6H_4NH_2$	HO-4-$C_6H_4NH_2$	HO-4-C_6H_4NHTMS	>99:1

hindered hydroxy moieties. For other cases, no noteworthy difference was noticed, and the selectivity reduces to moderate (entry 7) or low values (entries 8–10). For selective blocking of phenols in the presence of aromatic amines, successful experimentation was also set out using HMDS (entries 11–12). In both inter- (entry 11) and intramolecular (entry 12) competitive reaction, protection of the phenol groups solely found in short periods keeping the amine groups intact. Thus, this protection protocol of hydroxy group occurs with high yields (75%–99%) within 5–20 min without the need for additive or catalyst with the influence of ultrasonic irradiation [33].

6.2 *O*-Silylation of homoallyloxyalcohols

The thermal, physical, and chemical stability in a wide range of temperature and outstanding chemical resistance, auto-oxidizing capacity and very low surface tension, makes siloxanes and allyl ethers readily useful in radiation curing applications. Transition metal complexes, mainly ruthenium metal complexes catalyze the isomerization of allyl ethers to the corresponding 1-propenyl ethers for unmasking.

Lewis and Brønsted acids can initiate polymerization of the most reactive monomers of the 1-propenyl ethers by facile cationic photopolymerization. Urbala and Antoszczyszyn have synthesized allyl ethers—siloxane and allyl ethers—silyl ethers monomers under sonication in reasonable yield from their subsequent monoallyl ethers and chlorosilanes [34] (Scheme 13).

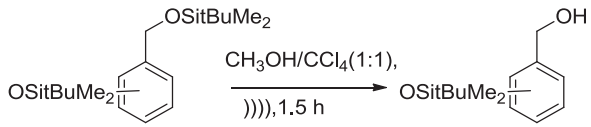


X = —$(CH_2)_n$—, n = 2, 3, 4, 5, 6; —CH_2—CH=CH—CH_2-,

Scheme 13 *O*-Silylation of homoallyloxy alcohols under ultrasonic irradiation.

6.3 Deprotection of silyl ether

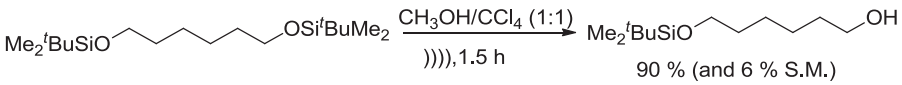
It has found that thermal cleavage of the silyl group requires harsh environments, but ultrasound promoted reactions proceeds in less time with high yield in a mixed solvent (Scheme 14) [35]. The experimental results revealed that primary *tert*-butyldimethylsilyl ether was removed selectively to the corresponding alcohol, whereas secondary and *tert*-butyl dimethylsilyl ethers remain stable. The cleavage reactions of *tert*-butyldimethylsilyl ethers of benzyl alcohols are brought off by use of a 0.25 M CH_3OH/CCI_4 (1:1) solvent mixture applying ultrasound energy for 1.5–3 h at 40–50°C in excellent yield (90%–96%) within a short time.



Scheme 14 Deprotection of hydroxy group of primary alcohol.

Under ultrasound irradiation, silyl ether in 1-*tert*-butyldimethylsilyloxy-6-*tert*-butyldiphenylsilyloxyhexane was chemoselectively deprotected affording desilylated product in 71% yield for 1.5 h, which increased to 90% upon 3 h sonication (Scheme 15).

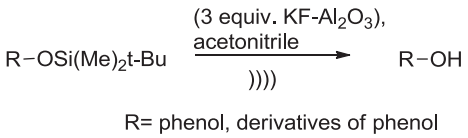
The Si—F attraction assists to deprotect *t*-butyldimethylsilyl (TBDMS) group, with the use of *tetra*-butylammonium fluoride (TBAF) as fluoride ion source through the breaking of Si—O bond.



Scheme 15 Selective cleavage of *tert*-butyldimethylsilyl ethers of primary hydroxy.

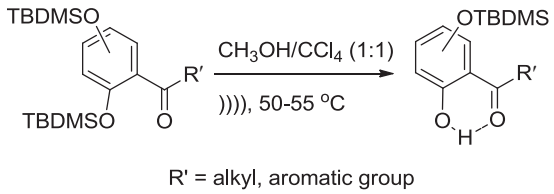
However, the shortcoming of TBAF is to encourage elimination reactions and this basic medium may also be troublesome for other protected functional groups such as benzoic and acetate groups. Added cleaving performances of trialkyl silyl ethers, such as AcOH/H_2O/THF, TFA/H_2O, I_2/MeOH, and K_2CO_3/MeOH have also been established, but these are specific to the individual substrates. Furthermost, this removal techniques face difficulty in aqueous workup and hence, a suitable and facile synthetic strategy for silyl ether cleavage from nucleosides is highly desirable in nucleoside chemistry.

Karimi and Golshani did the selective deprotection of *tert*-butyldimethylsilyl ethers of phenols by using potassium fluoride on basic alumina in acetonitrile under ultrasound, which is depicted in Scheme 16 [36]. Desilylation includes the nucleophilic addition of fluoride ion in the presence of basic species allied with potassium hexafluoroaluminate, potassium hydroxide, potassium aluminate, and potassium carbonate (KF-$A1_2O_3$). It was prevented by cooperative action of F^- ion on the alumina surface. Use of ultrasound with KF-based Al_2O_3 facilitated the reaction to furnish within a period of 15 min–4 h with good yield (70%–87%). High selectivity was noticed between TBDMS ethers of phenols versus benzyl alcohols as well as between SEM and TBDMS phenolic ethers under this neutral medium.



Scheme 16 Selective deprotection of *tert*-butyldimethylsilyl ethers of phenols with ultrasound.

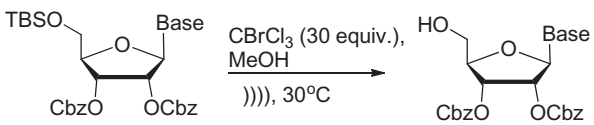
In synthetic chemistry, the orthogonal protection and deprotection among various functionalities ensure high priorities. Ultrasound-assisted selective removal of *tert*-butyldimethylsilyl ethers *ortho* to a carbonyl group was described by Alex et al. (Scheme 17) [37]. Highly regioselective cleavage at near to a conformationally fixed carbonyl group of aromatic and enolic *tert*-butyldimethylsilyl ethers using a straightforward ultrasound treatment in a CH_3OH/CCl_4 (1/1) mixture provided the targeted compounds. The reaction, in some cases quite longer due to the planar configuration of the carbonyl group relative to the *ortho*-silyl ether.



R' = alkyl, aromatic group

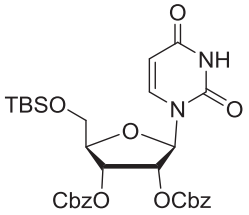
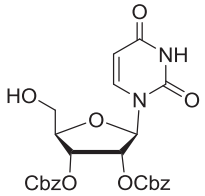
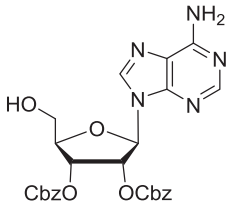
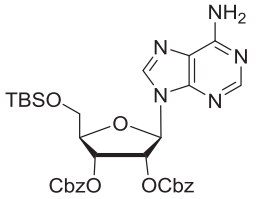
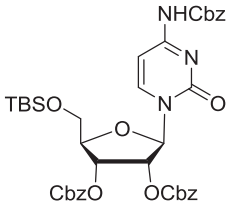
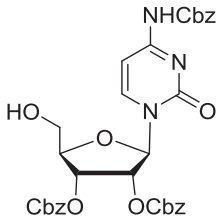
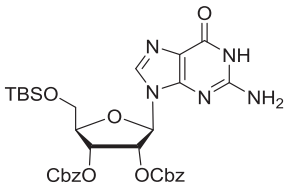
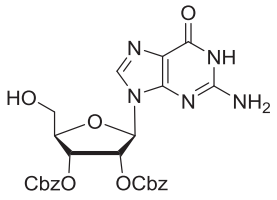
Scheme 17 Ultrasound-assisted selective desilylation of *tert*-butyl dimethylsilyl ethers.

The protection of hydroxy as silyl ether in nucleoside chemistry is a common concern, also to remove the TBDMS group, needs a suitable and selective procedure, to avoid side reactions, in particular, C—N bond cleavage. Jan et al. have demonstrated a milder approach for desilylation (Scheme 18) [38] as shown in Table 4, 2′,3′-*O*-bis (benzyloxycarbonyl) nucleosides, which upon exposure to bromochloromethane (30 equiv.) in methanol yielded products in 92%–96% within 30–50 min using ultrasound.



Scheme 18 Ultrasonic-assisted removal of the *tert*-butyldimethylsilyl group.

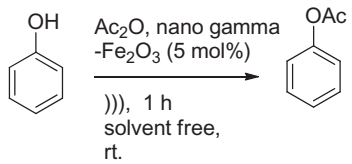
Table 4 TBS deprotection of the nucleoside bases in sonication conditions.

Entry	Starting material	Product	Time/min (heating at 60°C)	Yield (%)	Time/min (ultrasonic at 30°C)	Yield (%)
1			180	81	50	96
2			120	83	40	95
3			120	85	40	95
4			90	87	30	92
						

6.4 Acetylation

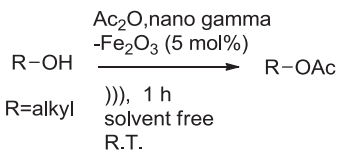
One of the most common and comprehensive methods in organic synthesis is the conversion of hydroxyl to acetyl derivative. The well-known *O*-acetylation proceeds generally with acetic anhydride in a wide range of solvents and catalysts. A diverse range of catalysts, particularly bases; 4-(dimethylamino) pyridine (DMAP), Lewis acids; $ZnCl_2$, zeolites; H-beta, enzymes; lipases are developed to assist these reactions. In recent days, metal triflates in ionic liquids have also been demonstrated as active catalysts for the acetylation with Ac_2O. Among these metal triflates are expensive; others are air and moisture sensitive and frequently require environmentally harmful volatile organic solvents, for example, dichloromethane and thus demand alternate procedure.

An exciting ecological process by Manohar et al., involves the application of γ-Fe_2O_3 nanoparticles as a recoverable and robust catalyst for the protection of phenol (1 mmol) with Ac_2O, (1.5 mmol) and nano-γ-Fe_2O_3 (5 mol%) for 1 h at r.t. under sonication (frequency 33 kHz and electric power 100 W) to get the desired acylated derivatives in an excellent yield (92%) (Scheme 19) [39].



Scheme 19 Iron oxide-NPs catalyzed acetyl protection of phenol under sonication.

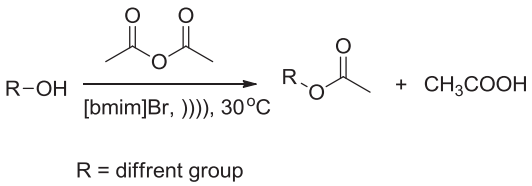
Even the substituted phenols were also acetylated, giving the corresponding products in excellent yields and the alcohols produced acetate derivatives in average yields (Scheme 20). Applying a similar methodology, the protection of hydroxy gave the desired products in 44%–96% yields. The high catalytic activity, low waste, low energy, and heat transfer efficiency compared to conventional heating, and recyclability of catalyst up to the fourth run makes this effort more advantageous.



Scheme 20 Iron oxide nanoparticles catalyzed acetyl protection of alcohol by sonication.

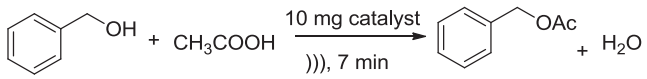
The sonochemical process was reported by Atul et al. for the acetylation of alcohols in ionic liquid at r.t. (Scheme 21) [40]. The reaction was performed applying sonochemical reaction of alcohol (10 mmol) with acetic anhydride (11.1 mmol) in ionic

liquid 1,3-di-*n*-butyl imidazolium bromide ([bbim]Br) for 5–95 min at 50 kHz and at 30°C, whereas without catalyst, the product resulted in moderate to excellent yield (59%–93%).



Scheme 21 Ultrasound-promoted acetylation of alcohols in ionic liquids.

A competent manner to acetylate alcohols was described by Sreedhar et al. in which exposure of the reactants to conventional heating or ultrasound (Scheme 22) [41] was carried out by using chamosite, as an active and reusable natural heterogeneous clay catalyst. The acylation was accounted for using carboxylic acid as an acylating agent. For instance, alcohol (1 mmol) and glacial acetic acid (2 mmol) (1:2 M ratio) were agitated under sonication using 10 mg of catalyst for about 5–40 min to acquire the pure product in the range of 60%–99% for individual alcohols.

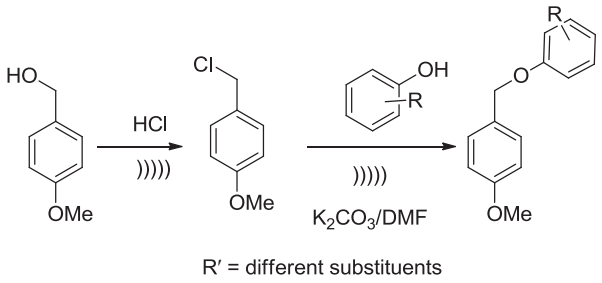


Scheme 22 Acylation of alcohols using heterogeneous catalyst and sonochemistry.

6.5 PMB/MOM protection

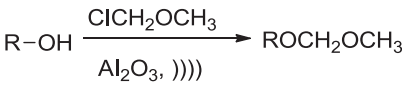
The 4-methoxybenzyl (PMB or MPM) group is another very common protecting group for phenols, alcohols, and nitrogen moieties [42] in organic chemistry. This is more robust and less expensive protecting group than many of the silicon-based protecting groups as the introduction happens with 4-methoxybenzyl chloride (PMB-Cl), which is comparatively safe and stable and can be removed by a varied type of reagents.

Experimentally PMB-Cl was synthesized from *p*-anisyl alcohol (1.61 mmol) followed by concentrated HCl (1.6 mL) under sonication, for 15 min to give the product in 75% yield with sufficient purity. Ultrasound-assisted PMB protection of various multisubstituted phenols, comprising sensitive phenolic aldehydes, is depicted in Scheme 23. Excellent yield (97%) is obtained within short reaction time (15 min) under sonication in comparison to a thermal condition which entails 17 h for this reaction. Herein, the use of ultrasound dealt conveniently concerning time although yields are not that much beneficial [43].



Scheme 23 Ultrasound-assisted PMB protection of multisubstituted phenols.

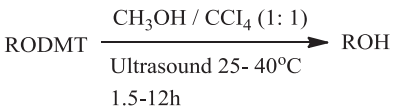
Hydroxy group protection as methoxymethyl ether (MOM ether) is a frequently used process in organic synthesis [42]. Ranu et al. stated an effortless and convenient procedure for the protection of a variety of alcohols without any solvent to obtain the corresponding methoxymethyl ethers in good yields (Scheme 24) [44] wherein hydroxy reacts with MOMCl on the alumina surface under ultrasound. Protection was carried out reasonably fast (1–24 h) and with high yields (68%–92%). Mild reaction medium evades any isomerization of double or triple bond in case of allylic and propargylic alcohols. Molecules like cholesterol and tetrahydrofurfuryl alcohols were also protected by this approach (hydroxy group). Tertiary alcohols are found inert to this procedure, which helps to protect primary and secondary alcohol selectively in the presence of tertiary alcohol group.



Scheme 24 Ultrasound-assisted MOM protection of hydroxyl group.

6.6 Deprotection of DMT (dimethoxytrityl)

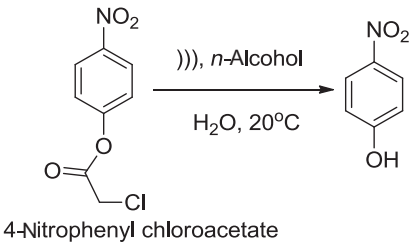
One of the routinely used protecting groups of hydroxyl is DMT, particularly applied during the preparation of antiviral, antibacterial, and anticancer agents. The conventional method for 5′-protection of nucleosides is the protection of the hydroxy group in the form of dimethoxytrityl [DMT] ethers. Acidic removal of dimethoxytrityl ether is usually performed with 80% acetic acid or 3% trichloroacetic acid, which affects acid-labile functionalities. Wang and McGuigan, have to get rid of the dimethoxytrityl group under sonication, using a mixed solvent of methanol and tetrachloromethane (Scheme 25) [45]. This technique is applicable for compounds having other functionalities like azide, acetyl, alkene, silyl, and internucleotide phosphate forming the parent primary alcohols in good [>90%] yield after 1–3 h. To a solution of DMT protected alcohol in tetrachloromethane and methanol mixed solvent (1:1 v/v) (10 mL) under ultrasonic bath was agitated for 3 h at 25–40°C to get primary hydroxy, protected dimethoxytrityl ethers in 69%–100% yields.



Scheme 25 Cleavage of the dimethoxytrityl group applying ultrasound.

6.7 Cleavage of phenol protected functionality

Upon neutral medium, hydrolysis of 4-nitrophenyl chloroacetate in the presence of 1 mol% of alcohol applying ultrasound at 25 kHz was carried out by Sander et al. (Schemes 26) [46] in the water at 20°C using cosolvent *n*-BuOH.

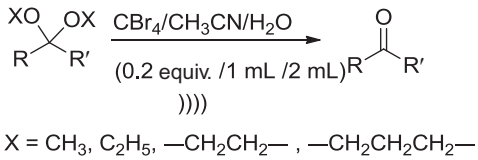


Scheme 26 Hydrolysis of 4-nitrophenyl chloroacetate by sonication acceleration.

7. Deprotection of carbonyl protecting groups

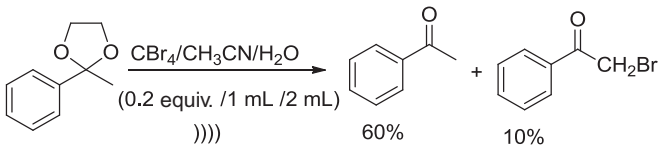
7.1 Removal of acetals and ketals

As it is well known that the transformation of carbonyl groups into the 1,3-dioxolane group is one of the most versatile used protective functionality for carbonyl group [47] and ultrasound assist more straightforwardly. The cleavage of acetals or ketals with protic acids such as CH_3CO_2H, HCI, oxalic acid, CF_3CO_2H, *p*-toluenesulfonic acid, Dowex-50 (acidic resin), SiO_2, Amberlyst-15, etc. are illustrious. Adam and Cheng hydrolyzed cyclic and acyclic acetals and ketals to their corresponding carbonyl compounds with catalytic CBr_4 in a mixed solvent CH_3CN/H_2O under sonication (39 kHz) at 45°C with low-to-good (25%–97%) yield (Scheme 27) [48].



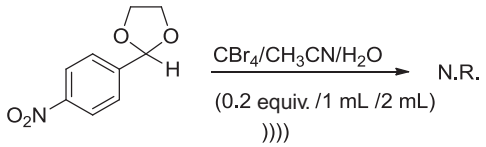
Scheme 27 Hydrolysis of acetals and ketals under sonication.

It has been observed that 2-(*p*-nitrophenyl)-l,3-dioxolanes and acyclic dimethyl acetal are thermally stable at a longer reaction time. To make it more convenient, a series of 1,3-dioxolanes was prepared in 60% yield along with a 10% yield of Et-brominated under sonication (Scheme 28) with 0.5 equiv. CBr_4 in CH_3CN/H_2O mixture for 3 h. Thus, this result is more promising than the protocol via thermal conditions.



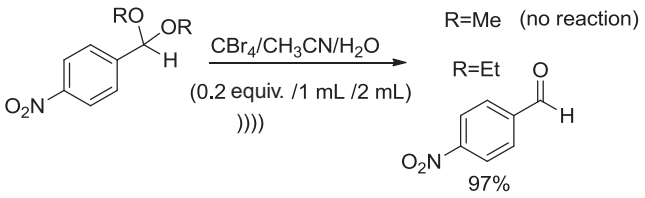
Scheme 28 Deprotection of 1,3-dioxolane under sonication.

The substituents group has a strong effect on the hydrolysis of 1,3-dioxolanes even under sonication reaction. Having weaker electron-withdrawing substituted carbonyl compound, like o-chlorobenzaldehyde acetal hydrolyzed slowly, but with a strong electron-withdrawing group, the same is resistant to hydrolysis under ultrasound (Scheme 29).



Scheme 29 Deprotection of aldehyde in the presence of ultrasonic irradiation.

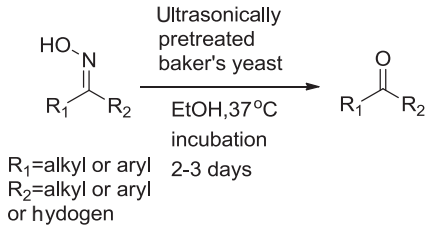
Remarkable selectivity was witnessed upon hydrolysis of acyclic dimethyl and diethyl acetals of *p*-nitrobenzaldehyde under ultrasonication as shown in Scheme 30. The highly chemoselective hydrolysis of the acetals of *p*-nitrobenzaldehyde was achieved in which only diethyl acetals was cleaved in 97% yield furnishing *p*-nitrobenzaldehyde after 4 h of sonication.



Scheme 30 Selective hydrolysis of acetals under ultrasonic irradiation.

7.2 Deprotection of aldehyde by deoximation of oximes

Reproduction of ketones from ketoxime/aldoxime is of prime importance during complex molecule synthesis. Most of the deprotection performances are relatively nonselective and inadequate whereas ultrasonically stimulated Baker's yeast in phosphate buffer, pH7.2, incubated at 37°C offered corresponding aldehydes and ketones in good yields from oximes (Scheme 31) [49]. A wide variety of oximes was converted to the corresponding aldehydes and ketones. Ultrasonic pretreatment of Baker's yeast enhanced the yields by c. 35% in a short period though sonochemically exploring Baker's yeast to crop almost quantitative regeneration of carbonyl compounds from their oximes (Table 5).



Scheme 31 Ultrasonic promoted deprotection of aldehyde by deoximation of oximes.

Table 5 Aldehyde/ketone product from deoximation under sonication.

Aldehydes and ketones	Yield (%) unsonicated after 3 days of incubation	Yield (%) sonicated after 2 days of incubation
Benzaldehyde	68	96
p-Methoxybenzaldehyde	72	98
Caproaldehyde	75	95
Acetophenone	56	63
Benzophenone	51	62
Cyclohexanone	65	87
Pinacolone	68	92
Camphor	76	97
Caprolactone	63	94
Butan-2-one	58	93

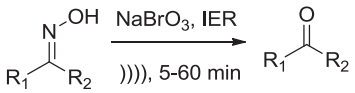
7.3 Rapid oxidative cleavage of oximes

The additional protecting group of the carbonyl are their oxime derivatives [50] which regenerate to parent aldehydes after cleaving the C═N bond without affecting the rest of the molecule.

Commercially available, stable, solid, capable of multielectron transfer reactions, and thermodynamically strong oxidant sodium bromate is used for this type of reaction.

Though sodium bromate is usually applied in aqueous media in the presence of co-reactants such as HBr, $NaHSO_3$, Br_2, $FeCl_3$, NH_4Cl, cerium(IV) ammonium nitrate, $KHSO_4$, H_2SO_4, $HClO_4$, and $[CH_3(CH_2)_3]_4NHSO_4$, unfortunately, the reaction conditions are hard, and particularly the removal of excess sodium bromate from the co-reactant is troublesome. Hence, the reactions were standardized by Shaabani et al. [51] (Scheme 32) using solvent-free ion exchange resin (IER) as cocatalyst in the presence of sodium bromate under ultrasonic irradiation to obtain parent carbonyl group in 84%–54% yields within 5–45 min at r.t.

The general experimental method was grinding a mixture of oxime (1 mmol), sodium borate (3.3 mmol), and ion exchange resin (0.2 g), applying sonication at 25–30°C for 15–30 min followed by washing with chloroform and purification by column chromatography.



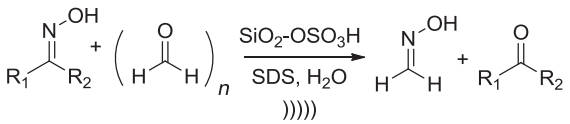
R_1 and R_2 = aryl and alkyl;
R_1 = aryl and R_2 = H.

Scheme 32 Ultrasound-promoted oxidative cleavage of oximes.

7.4 Silica sulfuric acid-catalyzed deprotection of oximes

There are several literature processes to furnish oximes other than carbonyl compounds such as oxidative deoximation, acid-catalyzed hydrolysis, reductive deoximation, and deoximation through the exchange of oximes with other carbonyl compounds. Sometimes these systems encountered drawbacks such as drastic conditions, requirements for refluxing temperature, long reaction times, tedious workup, undesired chemical yields, and use of toxic reagent.

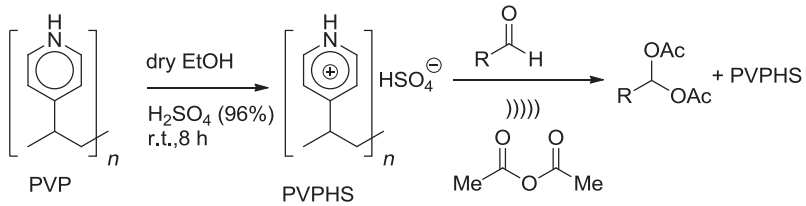
Silica sulfuric acid as stable, reusable, and cheap catalyst replaces sulfuric acid or chlorosulfonic acid as these are vicious for acid-sensitive functional groups. Silica sulfuric acid/surfactant/paraformaldehyde system, applying sonication remove oximes to their corresponding carbonyl compounds (Scheme 33) [52]. Silica sulfuric acid (0.25 mmol), SDS (5 mol%), and paraformaldehyde (2 mmol) were added to an aqueous solution of oxime (1 mmol) and sonicated at 25 kHz frequency at 50°C for 1–3 h, yielding aldehyde in 49%–97% yields.



Scheme 33 Deprotection of oximes to carbonyls under ultrasound irradiation.

7.5 Chemoselective 1,1-diacetate protection

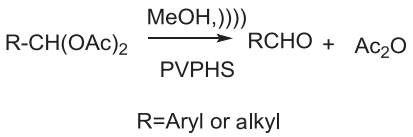
Used of solid acids as a heterogeneous catalyst in organic transformation are generally environmentally benign and less corrosion or avoid disposal of effluent. Acetals (1,1-diacetates) are frequently employed as a suitable protecting group for aldehyde owing to their significant stability to neutral and basic medium [53]. A simplistic process for protection and deprotection of aldehydes, catalyzed by PVPHS (Scheme 34) engaged in stirring of a mixture of aldehyde (1 mmol), PVPHS (5 mg, 0.01 mmol), and acetic anhydride (3.3 mmol) under ultrasonic irradiation at room temperature for 4–32 min yielding 72%–100% products.



Scheme 34 1,1-diacetate protection of aldehyde under sonication.

7.6 Deprotection of 1,1-diacetates

Unmasking of 1,1-diacetates to their corresponding aldehydes is a high concern, and several approaches have been published in the literature [54] (Scheme 35). The cleavage reaction involves sonication of a mixture of 1,1-diacetate (1 mmol), PVPHS (0.01 mmol) in methanol at ambient temperature for 10–80 min with moderate-to-high (76%–92%) yield.

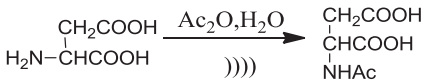


Scheme 35 Deprotection of 1,1-diacetates to parent aldehyde by sonication.

8. Protection and deprotection of amine group

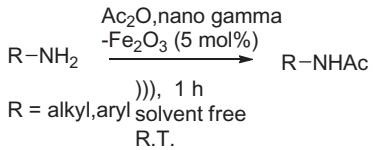
Protection of —NH_2 group is very much significant due to their presence in a diversity of biologically active compounds like amino acids, DNA base, etc. [55]. Amino acids are building blocks of proteins and peptides, neuropeptide [56], and fundamental priorities are the protection of amine functionality with various groups. In organic synthesis, a ubiquitous and necessary procedure to protect NH2 is amide formations which are useful building blocks to be utilized in pharmaceuticals, agrochemicals, and polymers industrially and academically.

Anuradha and Ravindranath described a strategy in which amino acids directly and rapidly acetylated at room temperature with acid anhydrides and activated esters in organic solvents (Scheme 36) [57] under sonication. For polar amino acids, water is added to facilitate the reaction's progress. Under this reaction methodology, to complete the reaction, it took 5 min for proline and 45 min for valine and isoleucine with producing products in 90%–99% yield. However, acetylation of tyrosine with acetic anhydride in dimethylformamide in moderate yield. The general procedure was trituration of amino acids (1 mmol) and Ac_2O (2 mmol) in ethyl acetate under sonication for the required period.



Scheme 36 Amino acids amine protection by sonication.

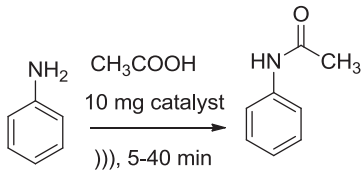
The acyl protection of various aromatic amines having electron-donating and electron-withdrawing groups were influenced by ultrasonic irradiation and iron oxide nanoparticle catalyst (Scheme 37) [39]. The typical reaction consists of agitation of a mixture of amine (1 mmol), nano γ-Fe_2O_3 (5 mol%), and acetic anhydride (1.5–3 mmol) under sonicator (frequency 33 kHz and power 100 W) to furnish the desired product in 28%–95% yields, according to the influence of the substituted group. The rates of yields are higher for aliphatic, cyclic, and heterocyclic amines with the advantage of a catalyst having recyclability up to the fourth run.



Scheme 37 Ultrasound-assisted iron oxide nanoparticles catalyzed acetyl protection of amines.

8.1 Ultrasound and heterogeneous catalyst promoted acylation of amines

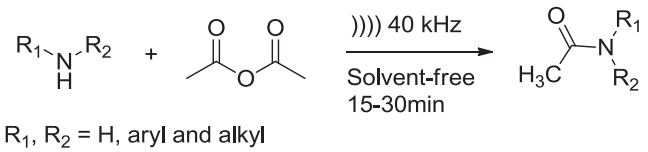
Efficient process to acetylate amines was reported by Sreedhar et al. in wherein (Scheme 38) [41] acylation was executed efficiently by naturally occurring clay chamosite, as an efficient and reusable heterogeneous catalyst along with an acylating agent. Glacial acetic acid (2 mmol) was added to amines (1 mmol) to a 2:1 M ratio in the presence of 10 mg of catalyst for about 5–55 min under sonicated in 30%–100% yields for different amines.



Scheme 38 Acylation of amines under catalysis and sonication.

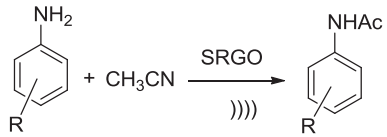
In particular, the synthesis of *N*-acetyl sulfonamides was carried out by the condensation of the various sulfonamides with anhydride or acyl chloride in the presence of a base. The similar acylation of sulfonamides was also accomplished with concentrated H_2SO_4, Lewis acids or heterogeneous solid acid in acetonitrile, palladium-catalyzed acylation of aryl with sulfonamides etc. under ultrasound. Recently, productivity for acylation of sulfonamides with the assistance of solid acid catalyst $H_6P_2W_{18}O_{62}$ in acetonitrile is recognizable.

Structurally diverse amine was acetylated efficaciously with acetic anhydride at room temperature without using solvent and catalyst under ultrasonic irradiation as described by Bouasla et al. (Scheme 39) [58]. Herein, a mixture of amine or sulfonamide derivatives (1 equiv.) and acetic anhydride (1 equiv.) were agitated under sonicator bath (frequency 40 kHz and nominal power 260 W) for 15–30 min to offer the *N*-acetyl amines in reasonable yield.



Scheme 39 Catalyst-free *N*-acylation of amines under ultrasonic irradiation.

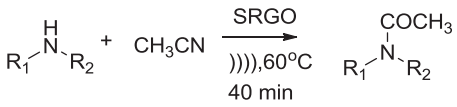
The amide formation finds the use of acyl halides, anhydride, and esters, but acyl halides and anhydrides are moisture sensitive and react very fast with water and alcohols forming acids and esters as by-products, interfering in the purification of the desired amides. These amide formations require bases like imidazole and pyridine to perform the reaction. To avoid these, sulfonated reduced graphene oxide (rGO-SO_3H, SRGO), as a reusable, metal-free, solid acid catalyst was employed for the direct *N*-acetylation of amines in acetonitrile under irradiation into the corresponding amides, avoiding toxic and moisture sensitive substances such as acetyl chloride, acetic anhydride, and acetic acid (Scheme 40) [59]. 0.05 g of SRGO catalyst was added to a mixture of amine (1 equiv.), and acetonitrile (1 equiv.) and sonicated at 50–60°C to furnish the reaction in 80%–98% yields in less than 1 h.



(frequency of 20 kHz and 100% output power)

Scheme 40 *N*-Acetylation of amines with acetonitrile by SRGO catalyst under sonication.

Moreover, primary and secondary amines (Scheme 41) were also protected without the use of toxic reagents to formulate several *N*-acetamides.

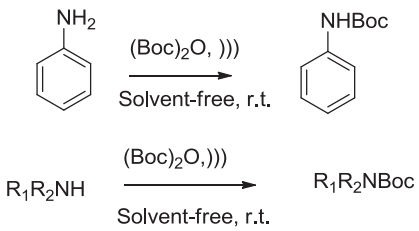


Primary amine: R_1= Phenyl, R_2= H
Secondry amine: R_1= Alkyl, R_2= Alkyl

Scheme 41 Protection of primary and secondary amine by sonication.

8.2 *N*-Boc protection of amines

The *tert*-butyloxycarbonyl (Boc) group is very common, protecting the functionality of amine by base-catalyzed reactions using aq. NaOH, DMAP, NaHMDS, or Lewis acids catalyzed reactions, such as $ZrCl_4$, $HClO_4/SiO_2$, $Cu(BF_4)_2{\cdot}9H_2O$, $LiClO_4$, $Zn(ClO_4)_2{\cdot}6H_2O$, $La(NO_3)_3{\cdot}6H_2O$, yttria-zirconia, amberlyst-15, $H_3PW_{12}O_{40}$, montmorillonite K-10, and sulfamic acid. Nonetheless, due to acidity, corrosiveness, toxicity, high cost, and requirement of other auxiliary substances during isolation of the product, a green and simple approach for the *N*-Boc protection of various amines under ultrasound irradiation was established by Amira et al. (Scheme 42) [60]. The reaction of primary and secondary aromatic and aliphatic (cyclic and acyclic) amines (1 mmol) with



R_1 and R_2= H, alkyl, or aryl

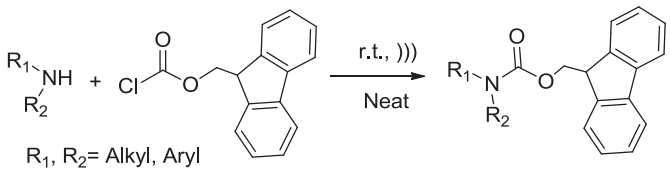
Scheme 42 *N*-Boc protection of amines under ultrasonic irradiation.

di-*tert*-butyl dicarbonate (1.1 mmol) without using any solvent or catalyst formed compound within 2–7 min quantitatively. Similarly, the amine functionality of β-amino alcohol, α-aminoesters, and sulfamines were protected excellently with preservation of stereochemistry of *N*-Boc amino acids (Scheme 42) in a FUNGILAB ultrasonic bath (40 kHz, 250 W) with neat $(Boc)_2O$.

8.3 *N*-Fmoc protection of amines

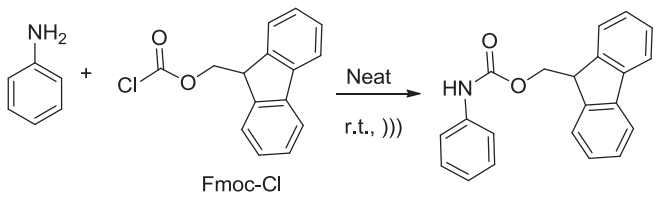
Another typical amine protecting functionality is Fmoc group, and the introduction of this functionality is eased by coupling an $—NH_2$ with an activated 9-fluorenylmethyl carbonate such as Fmoc-chloride (Fmoc-Cl), Fmoc benzotriazole-1-yl carbonate (Fmoc-OBt), or (9-fluorenylmethoxycarbonyloxy) succinimide (Fmoc-OSu). The most important is their stability toward acidity, facilitating the selective removal of other common groups Boc under acidic exposure. Fmoc groups are deprotected with primary amines (e.g., cyclohexylamine and ethanolamine), secondary amines (e.g., piperidine and piperazine), and tertiary amines; the removal of this group is fast with secondary amines but comparatively slower with tertiary amines.

A simple and sustainable method under ultrasonic irradiation for the *N*-Fmoc protection of structurally variant primary and secondary amines was described by Rachida Mansouri et al. (Scheme 43) [61]. The reactions occur with reasonably good yield (72%–95%) and short reaction time (2–5 min).



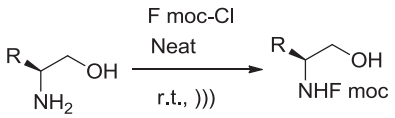
Scheme 43 Fmoc protection of primary and secondary amines by sonication.

Aniline amine protection as *N*-Fmoc with Fmoc-Cl in dichloromethane, under ultrasonic irradiation, occurs in 3 min with a yield of 95%, and comparable yields are obtained even in the absence of solvent. Scheme 44 indicates that ultrasound, rather than solvent, plays a more prominent role.



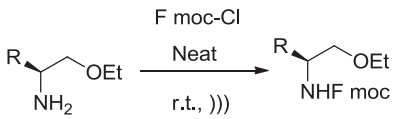
Scheme 44 *N*-(9-Fluorenylmethoxycarbonyl) protection of aniline.

The modification of functional groups of amino acids and their derivatives is always a significant concern because of their importance in peptide synthesis. The Fmoc protection accomplished products in the range of 85%–92% yields only after 2 min of reaction (Scheme 45).



Scheme 45 F-moc protection of β-amino alcohols by sonication.

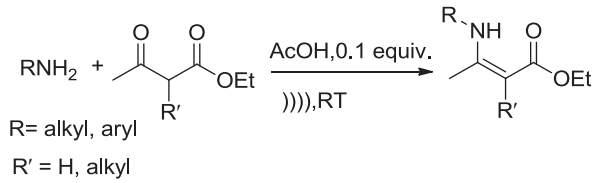
α-Amino acids are protected without using solvent for 2–5 min under sonication of amine (1 mmol) and Fmoc-Cl (1.1 mmol) at room temperature in good to excellent yields as described in Scheme 46. The experimental results conclude that the yield is independent of the nature of aromatic substituents.



Scheme 46 F-moc protection of α-amino acid esters by sonication.

8.4 Ultrasound-assisted amine protection as β-enamino esters

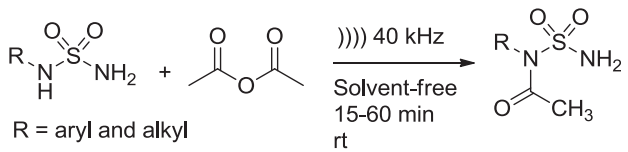
β-Enaminones are one of the fundamental and useful scaffolds for the synthesis of biologically active analogues. It is synthesized from β-dicarbonyl compounds by utilizing Al_2O_3, SiO_2, montmorillonite K-10, and $NaAuCl_4$ as catalysts. To avoid the hazardous solvents, costly reagents, longer reaction times, etc. Carlos et al. applied environmentally friendly and very fast and mild procedure using acetic acid as an acid catalyst operating ultrasound irradiation (Scheme 47) [62]. To protect amines in the form of β-enamino esters, a mixture of β-dicarbonyl derivatives (2 mmol), amines (2 mmol), and AcOH (0.2 mmol) were shaken under irradiation at 40 kHz and with 100 W power at a temperature below 30°C for 0.2–3 h, contributing the product in moderate to almost quantitative yield (60%–98%).



Scheme 47 Ultrasound-assisted amine protection as β-enamino esters.

8.5 *N*-Acylation of sulfonamides

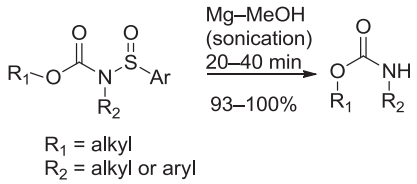
Acetylated sulfonamides moieties (*N*-acetyl sulfonamide) are present in several important biomolecules [63]. Greener approach has been informed by Bouasla et al. for acylating the sulfonamide group under ultrasonic irradiation without catalyst use (Scheme 48) [58]. To synthesize *N*-acyl sulfonamides in good yields, a mixture of sulfonamide derivatives (1 equiv.) and Ac_2O (1.0 equiv.) was sonicated at a frequency of 40 kHz and power 260 W for 15–60 min at r.t.



Scheme 48 Catalyst-free *N*-acylation of sulfonamides under ultrasonic irradiation.

8.6 Deprotection of substituted phenyl sulfonyl carbamates

To furnish parent amide compound, arene sulfonamides was cleaved under sonication (Scheme 49) [64] using Mg powder (2.5 mmol), arene sulfonamides (0.5 mmol) in MeOH (6 mL) for 20–40 min to get white crystalline product quantitatively with 81%–100% yield. The conventional manner takes a longer time to complete this reaction (6–24 h). It was observed that (i) Mg- powder (5 equiv.) are satisfactory for an effectual removal of 4-$BrC_6H_4SO_2$, $PhSO_2$, Ts, and Cbs groups; and (ii) 10 equiv. for the 2,4,6-$^{i}Pr_3C_6H_2SO_2$ and 2,4,6-$Me_3C_6H_2SO_2$ functionalities, whereas (iii) at least 15 equiv. for the demasking of the Mbs-carbamate.



Scheme 49 Removal of arene sulfonamides by use of magnesium and sonication.

8.7 Deprotection of propargyloxycarbonyl (POC) [65, 66]

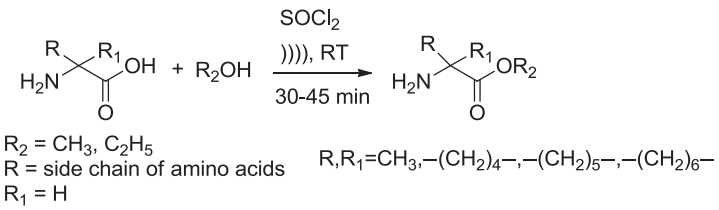
An uncommon protecting group for solution-phase peptide synthesis is propargyloxycarbonyl (POC). This functionality has sustainability toward the ^{t}Boc demasking and even acts as a safeguard to amino acid chlorides. The compounds having this group is also used for couplings on hindered amines without racemization. Chandrasekaran and group applied the ultrasonic irradiation for the deprotection of this functionality in tetrathiomolybdate complexes $[(PhCH_2NEt_3)_2MoS_4]$.

9. Carboxylic acid group protection/deprotection

Carboxylic acid protection/derivatization in peptides, protein or heteropoly acids, also in the manufacture of fine and specialty chemicals such as fragrances, pharmaceuticals, and pesticides is highly essential. Normally, the —COOH functionalities are blocked as ester and various routes are reported for their conversion. Traditional methods have few drawbacks like the use of gaseous HCl as a catalyst where possibilities of side-chain cleavage of amino acids glutamine and asparagine are possible. In that respect, mild and ultrasound approaches support to perform the reaction with good yields.

9.1 Esterification of —COOH in amino acids

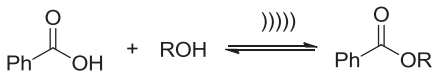
Proteinogenic and α,α-dialkylaminoacid ester salts were derived by ultrasonic irradiation for esterification of varied amino acids (Scheme 50) [67] using freshly distilled $SOCl_2$ (1.3 mL, 11 mmol) at −10°C in dry methanol or ethanol at room temperature for 30–45 min. The reactions produced esters in good yield (94%–98%).



Scheme 50 Esterification of amino acids under ultrasound irradiation.

Solid acid catalysts like zeolites, clays, etc. facilitate the esterification. The activated carbons as porous materials are broadly explored as adsorbents, catalysts, or catalyst supports and their acidic and basic properties depend on their origin and on the temperature as well as conditions under which these are activated.

Nevskaia et al. in their work used HNO_3-oxidized activated carbon as a catalyst for the esterification of benzoic and phenylacetic acids with alcohols under ultrasound irradiation (Scheme 51) [68]. This catalytic system esterifies organic acids like carboxylic and phenolic hydroxy groups with alcohols on the carbon surface. For esterification, the carboxylic acid (benzoic acid or phenylacetic acid) was mixed with alcohol without any solvent and then sonicated in the ultrasonic bath (Selecta Ultrasound-H) at 40 kHz and 550 W and 333 K for 11 h. The esterification of benzoic and phenylacetic acids with alcohols was successfully furnished on nitric acid-oxidized carbon under ultrasound acceleration with yield ∼85% and high selectivity (∼95%).



Scheme 51 Esterification of benzoic and phenylacetic acids under ultrasound irradiation.

The widely applicable reactions to esterified carboxylic group(s) [69] comprise through the alkylation of carboxyl oxygen or a nucleophilic substitution on the carboxyl carbon. In addition to iodomethane, other reagents such as trimethylsilyldiazomethane, diazomethane, and polymer-supported methyl sulfonate, dimethyl sulfate, and dimethyl carbonate are used as electrophilic methyl group equivalents. Among several, Fisher esterification is the most familiar classical approach for such conversion. These methyl esterifications find many applications containing biodiesels synthesis, fragrance materials and surfactants along with purification, characterization of structurally complex molecules [70], and so on. Typically, these reactions are acid-catalyzed and necessities of the excess of alcohol for higher yields, also, due to the employment of acidity, the susceptibility of acid-sensitive functionalities is quite less. Sonication finds much promising alternative to the traditional esterification process concerning functional groups compatibility and selectivity (Fig. 7).

To circumvent this problem, a single step methyl esterification applying catalytic quantities of the polymer-bound phosphine TCT/PS-Ph_3P/Na_2CO_3 combination (1:0.1:2 M ratio) in methanol (0.5 mL) at 50°C under ultrasonic irradiation was done under sonication to get the ester in moderate-to-high (70%–98%) yield within 10–30 min. This weakly basic system enables reaction compatibility with a range of acid- or base-sensitive functional groups of carboxylic acids like a reactive hydroxy group and different *N*-protected α-amino acids [71].

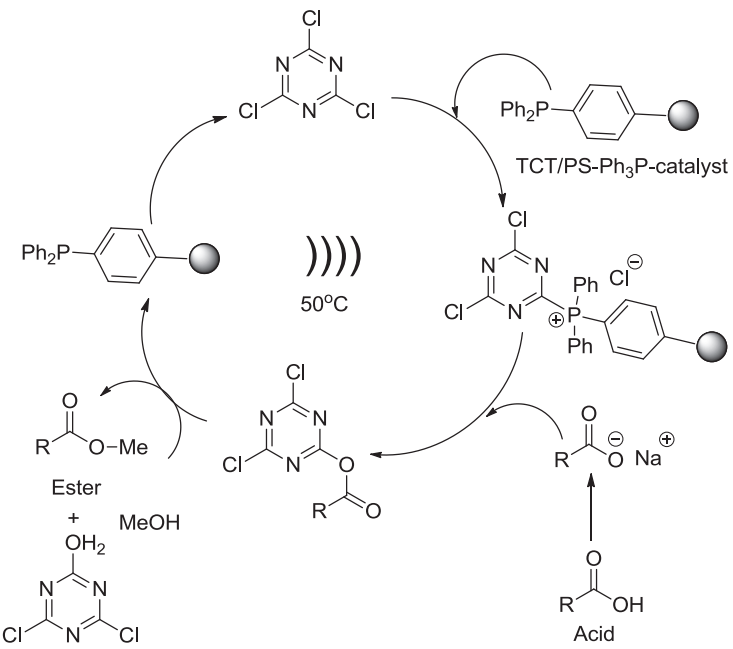
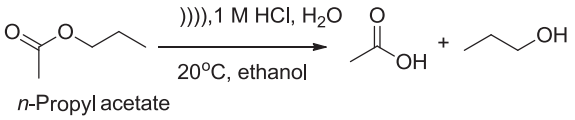


Fig. 7 TCT/PS-Ph_3P-catalyzed methyl esterification.

9.2 Ester hydrolysis in the presence of sonication

In a binary solution comprising ethanol-water, acidic hydrolysis of *n*-propyl acetate was executed with 1 M HCl at 20°C applying ultrasound at 22 kHz (Scheme 52) and the progress of the reaction was monitored by GLC [46]. The experimental result reveals that the effect of sonication is chain length depended, and it is higher for ethyl and propyl, indicating solvent interaction of ester. In the case of hydrophobic compounds, the hydrolysis requires cosolvent.



Scheme 52 Acid-catalyzed hydrolysis of *n*-propyl acetate by sonication acceleration.

10. Summary

In conclusion, this chapter included the surveys and summaries of previously published studies related to the protection and removal of majorly used functional groups such as amine, hydroxy, carboxyl, carbonyl, amide, and so on under environmentally friendly ultrasound-assisted protocols. The poor yields in traditional methods, the use of expensive catalysts, longer reaction time and limited scope of substrates urged to look for a high-yielding, expeditious, mild, and easy to handle mode triggered by an alternative sonication-mediated energy as an advantageous strategy in synthetic chemistry. In this chapter, the mechanism of sonication is pictorially depicted with brief discussion for lucid understanding to the researchers in the relevant field. Herein, under sonication, the detailed deliberations on the ultrasound-promoted protection and deprotection of hydroxy group (—OH) in carbohydrates such as acetyl and removal of ketal, acetal, acetate, trityl, and benzylidene functionalities and the migrations of a few functional groups and the removal of terminal acetonides in carbohydrates are conferred.

On the other hand, the same energy source showed its potentiality to furnish the protection and deprotection of hydroxy group in noncarbohydrates as a silyl ether, acetyl ester, PMB/MOM ether, etc. mildly. Deprotection of acetal, ketal, and oxime protecting groups of carbonyl functionality as well as chemoselective 1,1-diacetate protection and deprotection are also summarized. Besides, the protection of amine group as *N*-acetyl, *N*-Boc, *N*-Fmoc as well as β-enamino esters, *N*-acetyl of sulfonamides and the several deprotection of amine functionality are covered. Esterification of carboxylic acid in amino acids and its hydrolysis under sonication has also elaborated in this article. In the end, it has been realized that for most of the protection and deprotection of the functional groups, the reactions under sonication took less time and provided excellent yields in comparison to the traditional ones. Hence, the readers, researchers, and academicians might be benefited from this assembled literature data for the future applications of ultrasound in organic reactions.

Acknowledgments

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CHAPTER 9

Sonochemical protocols for Grignard reactions

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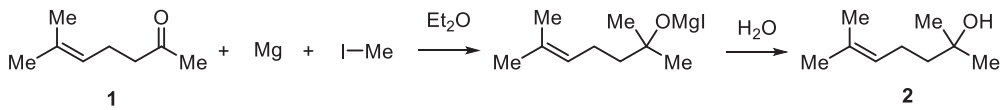
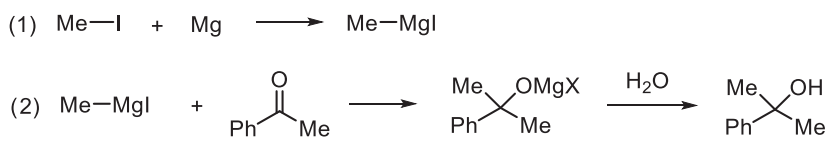
1. Introduction

Inspired by zinc-organic chemistry actively explored in the end of 19th century at the laboratory of Russian chemist Aleksandr Mikhailovich Zaitsev (Saytzeff), Philippe Francois Antoine Barbier (1848–1922) and his doctoral student Francois-Auguste Victor Grignard (1871–1935) attempted to perform a one-step synthesis of alcohol **2** using ketone **1** and methyl iodide by replacing zinc in the Wagner and Saytzeff method [1] with magnesium (Scheme 1) [2]. This reaction, nowadays known as the Barbier reaction, initiated more intensive research in organomagnesium chemistry. The organometallic species in this process are conveniently generated in the reaction in situ. However, the one-pot process in the Barbier reaction does not always involve the formation of organomagnesium halides as intermediates [3], resulting in low specificity and overall unsatisfactory outcome of the reaction for many substrates [4]. Therefore, a two-step approach, which involves initial preparation of organomagnesium halides followed by their reaction with carbonyl substrates, was developed by Grignard in his doctoral thesis [5]. In his seminal work [6], Grignard exemplified this process using the reaction of methyl iodide with magnesium and then the reaction of acetophenone with the resulting methylmagnesium iodide (Scheme 2). Other successful examples reported in this publication [6] included the reaction of isobutylmagnesuim bromide with benzaldehyde and that of benzylmagnesium bromide with acetone.



Scheme 1 Barbier reaction.



Scheme 2 Grignard reaction.

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https://doi.org/10.1016/B978-0-12-819540-6.00009-7

This reaction of organomagnesium halides with carbonyl compounds is now known as the Grignard reaction, while organomagnesium halides, separately prepared in this method before their reaction with carbonyl compounds, are called Grignard reagents [7]. The Grignard reaction has been used widely in the preparation of various valuable products and intermediates. The importance of this reaction was well recognized and in 1912 Grignard was awarded with the Nobel Prize in Chemistry.

2. Grignard sonochemistry

Many ultrasound methods have been used in organic synthesis and there is a clear trend in developing more ultrasound-based protocols for new and classical reactions [8]. Ultrasound applications in organic synthesis have gained interest due to their high efficiency, relatively inexpensive equipment, simple procedures, and sustainability. The prevalent trend toward sustainable approaches demands advanced ultrasound-assisted protocols for greener synthetic methods [9]. Despite many successful applications [10], organometallic applications in sonochemistry are relatively limited and yet to come. This chapter focuses on advancements in the ultrasound-assisted protocols for the preparation of Grignard reagents and ultrasound-promoted Grignard reactions.

2.1 Ultrasound-assisted preparation of Grignard reagents

The history of ultrasound applications in organometallic chemistry began in 1950, when Renaud reported [11] the first protocol for organometallic reagent preparation in ultrasonic baths. This work described the preparation of Grignard reagents and organolithium compounds, but the fundamental aspects of the method and role of ultrasound remained unexplored.

An attempt to continue further from the Renaud's success and expand this field of organometallic chemistry was made by Luche and Damiano in 1980 by performing another study on the formation of organolithium compounds under ultrasound irradiation [12]. Surprisingly, almost instant initiation of the reaction was observed even in solvents of commercial grade without any additional drying. That outcome was unachievable in such solvents under conventional conditions. To explain the successful formation of organolithium compounds, two possible roles of ultrasound waves were proposed: mechanical and cleansing effects.

Howkins et al. [13] published their research shedding light on the influence of ultrasound on metal surface. The beneficial effect of ultrasound irradiation was explained by the cavitation activity, which created bubbles drilling holes on the metal surface. The metal erosion was associated with the cavitation "collapse" phenomena, an implosive high-energy effect of expansion and compression of sound waves in a locally enhanced sound-pressure field. Although, this work did not directly describe the Grignard reagent formation, it opened a route to further investigations of metal surface related processes.

The role of metal surface in Grignard reagent formation was elegantly explored by Whitesides' Research Group [14], which developed a practical way to increase the rate of solid-liquid reactions between magnesium and organic halides. To study the processes undergoing in the reaction mixture, they prepared exceptionally pure magnesium crystals (99.999%) and examined the surface halide-metal interactions. It was found that initiation of the reaction took place at the induction period when tiny corrosion pits and dislocations were formed inside the metal lattice. The localized pits in the metal surface were formed in the first phase of reaction, which was defined as an activation period. With the pits growing and overlapping, the second phase started and the reaction became self-sustained. The Grignard reagent formation was found to depend entirely on the rate of occurrence of pits and dislocations. Subsequently, surface area was confirmed to be the major factor determining the reaction rate in the Grignard reagent synthesis with ultrasound helping to increase this surface area on magnesium particles.

Another vital impact on the field was made by Hoffmann's group [15], which studied the fundamental kinetic processes occurred in the local ultrasound-produced bubbles creating microjets at the metal surfaces. Several models for the Grignard reagent formation were created to describe relationships between the metal activation degree and ultrasound field local energy spreading. The results obtained in this study made it possible to predict the reaction rate for the Grignard reagent formation on the basis of the solid-liquid interaction model.

It was demonstrated that a combination of calcium and magnesium could improve yields of Grignard reagent under ultrasound protocols. This effect was attributed to the brittle alloy structure, which could be easily cleaved by the ultrasound force, achieving significantly active small magnesium particles, while calcium remained intact. It was shown that applied together, ultrasound and MgCa alloy could significantly reduce the formation of undesirable admixtures during the reaction (Table 1).

Table 1 Formation of benzylmagnesium chloride and by-products from benzyl bromide and the metal in THF at 5°C.

Application	BnMgCl (mol%)	$PhCH_2CH_2Ph$ (mol%)	Toluene (mol%)
Mg without ultrasound	61	10.2	16.8
Mg with ultrasound	75	2.8	12.4
MgCa with ultrasound	95	0.6	2.4

The benefits of using MgCa alloys in the ultrasound-promoted synthesis of various Grignard reagents have been well explored [16, 17]. Besides the synthesis of typical Grignard reagents, the application of MgCa alloys opened a route to the engagement of highly inactive halides in the formation of organomagnesium halides [15]. Thus, phenyl fluoride was utterly unreactive and the standard method [18] for the preparation of

phenylmagnesium fluoride was extremely time consuming, complicated, and occasionally ineffective. However, the combined application of MgCa alloy and ultrasound irradiation made this reaction possible (Table 2) [15].

Table 2 Formation of phenylmagnesium fluoride in the reaction of phenyl fluoride with magnesium and magnesium calcium alloy in THF at 60°C after 15 h.

Metal	PhMgF yield (%) with ultrasound	PhMgF yield (%) without ultrasound
Mg	0.6	≈0
MgCa	8	≈0

The effect of ultrasound on magnesium reactivity was studied by Sprich and Lewandos [19] using a model reaction of 2-bromopentane with magnesium turnings in diethyl ether containing different amounts of the water/alcohol contamination. They observed that ultrasound irradiation did not affect yields but significantly reduced the initiation time of the reaction. Similarly, in the reactions of chlorocyclohexane and 1-bromonaphthalene with magnesium, a substantial reduction of the time needed to initiate a self-sustaining reaction was observed under ultrasonic irradiation [20]. Sprich and Lewandos [19] attributed the improved initiation of the reaction to the "cleaning" role of low-intensity sonication via removal of a thin layer of water or alcohol adsorbed onto the magnesium surface. However, Teerlinck and Bowyer [21] examining the effects of magnesium surface on the formation of Grignard reagents found that ultrasound irradiation of magnesium in dioxane prior to the reaction with organic halides did not significantly benefit the process [22].

It was demonstrated that ultrasound irradiation frequency played an important role in the acceleration of the Grignard reagent formation [23]. Changing the frequency from 44 to 22 kHz nearly doubled the rate of the reactions of vinyl chloride and chlorobenzene with magnesium in THF. Importantly, no products of the Wurtz side reaction were detected when these reactions were carried out under sonication.

An important contribution to understanding the ultrasound effect in the process of the Grignard reagent formation was made by researchers from the University of Tartu [24, 25]. They studied a role of ultrasound in the formation of Grignard reagents investigating the effects of reaction inhibitors (water and alcohol) on the kinetics of induction period. A direct correlation was found between the concentration of inhibitors and the initiation constant rate. However, when the process occurred under ultrasound irradiation, even a significant amount of inhibitors (40–50 mM water) did not stop the formation of Grignard reagents. Without sonication, the reaction, under otherwise identical conditions, did not even start.

Interesting results were obtained when toluene or its mixtures with THF or diethyl ether were used as solvents for the Grignard reagent preparation [24]. A substantial

acceleration of the reaction was observed under ultrasound irradiation in toluene in the presence of THF (Table 3). Similar results were also obtained for the toluene—diethyl ether mixtures [24, 25]. It should be noted that the initiation of the Grignard reagent formation was accelerated by ultrasound in pure diethyl ether a few times less compared to the reaction in toluene in the presence of diethyl ether. This fact was associated with the higher cavitation collapse energy in toluene compared to that in ether. Therefore, the magnesium oxide contaminants situated on the metal surface could be removed faster. It is also worth noting that comparison of the yields proved lack of an ultrasound influence on the chemical nature of the process, since in all cases the outputs were almost identical

Table 3 Rate constants for the slow stage of the formation of alkylmagnesium bromides in toluene in the presence of THF (0.51 M).

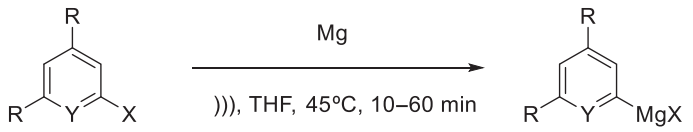
R–Br + Mg ⟶ R–MgBr

	$k \times 10^4$ (mol dm^{-3} s^{-1})[a]	
R	**With sonication[b]**	**Silent[c]**
Et	0.73	0.17
n-Bu	0.83	0.098
i-Bu	0.52	0.090
s-Bu	0.61	0.08

[a]Average values of several determinations.
[b]Mean error about ±10%.
[c]Mean error about ±15%.

and only initiation constant and induction period were affected by ultrasound.

An efficient ultrasound-assisted protocol for the preparation of Grignard reagents was developed using aryl and heteryl halides reactions with magnesium in dry THF [26]. The quantitative conversion and yields of Grignard reagents **3**–**6** were obtained when 2-bromopyridine, 2-chloropyridine, bromobenzene, and 1-bromo-3,5-dimethoxybenzene were used as substrates in the ultrasound protocol (300 kHz, 200 W) (Scheme 3). However, this reaction failed when these conditions were applied to chlorobenzene or when the reactions of 2-chloropyridine or 1-bromo-3,5-dimethoxybenzene were carried out at lower



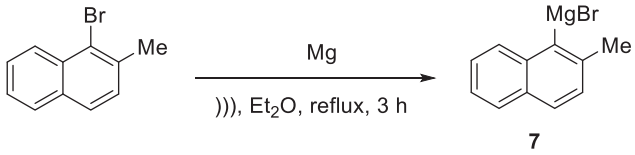
3–6 (100%)

X = Br, Y = CH, R = H (**3**), OMe (**4**); Y = N, R = H (**5**);
X = Cl, Y = N, R = H (**6**)

Scheme 3 Ultrasound-assisted synthesis of (het)arylmagnesium halides **3**–**6**.

frequencies (19.6–35 kHz). Instead, the formation of a substantial amount of Wurtz reaction side-products was detected.

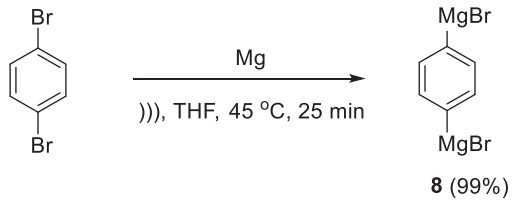
The synthesis of Grignard reagent **7** from 1-bromo-2-methylnaphthalene and magnesium turnings in diethyl ether (Scheme 4) was facilitated by sonication in the cleaning bath (41 kHz, 53 W) [27]. The reaction was effectively completed in 3 h affording the



Scheme 4 Ultrasound-promoted preparation of 2-methyl-1-naphthylmagnesium bromide (**7**).

solution of **7** suitable for the following steps in the synthesis of 1,1′-binaphthyl-2-carboxylic acid.

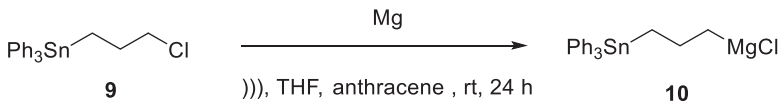
It was also reported [28] that 1,4-dibromobenzene in the reaction with magnesium in THF under ultrasonic irradiation was nearly quantitatively converted to the corresponding



Scheme 5 Reaction of 1,4-dibromobenzene with magnesium under sonication.

Grignard reagent **8** (Scheme 5). The latter was used for further silylation with dimethylsilyl chloride at both reactive sites.

The ultrasound-promoted preparation of Grignard reagent **10** was reported [29] from (3-chloropropyl)triphenylstannane (**9**) and magnesium in the presence of catalytic



Scheme 6 Synthesis of organotin Grignard reagent **10**.

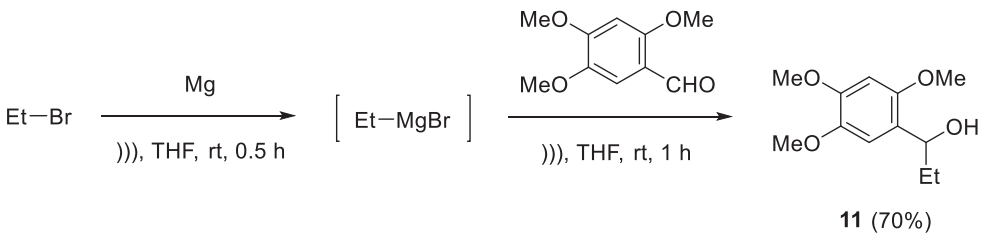
amounts (20 mol/%) of anthracene in THF (Scheme 6). The obtained Grignard reagent **10** was effectively used for further transformations.

Overall, ultrasound was found to be beneficial for the promotion of Grignard reagent formation. The developed ultrasound protocols were rather general and practical allowing fast initiation of reactions without the use of dry solvents and affording alkyl and arylmagnesium halides in good yields. Even though various ultrasound-generating devices were found to be suitable for the reaction, attention should be paid to the frequency of ultrasound irradiation. Variations in the frequency and power might result in a dramatic difference in the reaction product composition and yields.

2.2 Reactions of Grignard reagents under ultrasound irradiation

2.2.1 Reaction of Grignard reagents with aldehydes

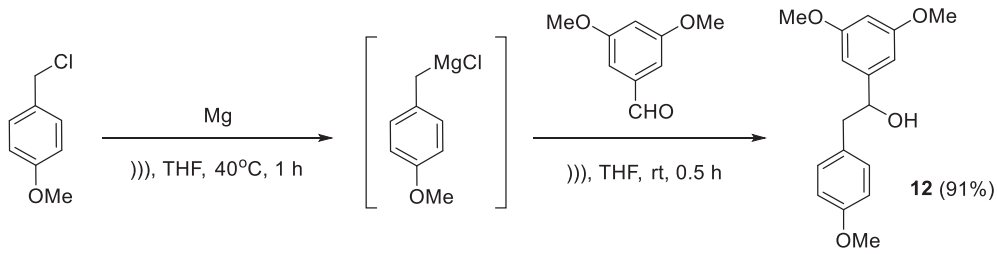
Often, sonication is also utilized in subsequent reactions of Grignard reagents after their preparation under ultrasound irradiation. This approach was applied for the synthesis of several natural product intermediates and bioactive compounds. Particularly, in the synthesis of α-asarone, ethylmagnesium bromide was prepared in THF under ultrasound



Scheme 7 Grignard reagent in the ultrasound-assisted synthesis of an α-asarone precursor.

irradiation (Scheme 7). In the following sonicated step, ethylmagnesium bromide was involved in the reaction with 2,4,5-trimethoxybenzaldehyde to afford alcohol **11**, which was further dehydrated to α-asarone [30].

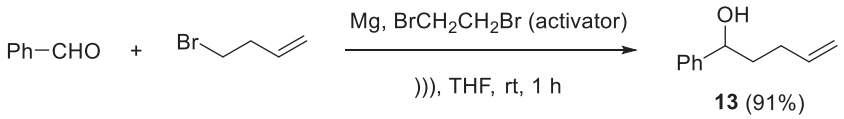
A similar protocol was applied for the synthesis of another natural product, resveratrol. Initially, *p*-methoxybenzyl chloride was converted into the corresponding Grignard reagent, which was further used for the reaction with 3,5-dimethoxybenzaldehyde to



Scheme 8 Grignard reagent in the ultrasound-assisted synthesis of a resveratrol precursor.

afford alcohol **12** in good yield (Scheme 8). Both steps were conveniently performed under ultrasound irradiation (500 W) in THF [31]. Alcohol **12** was further dehydrated and demethylated to produce the desired resveratrol.

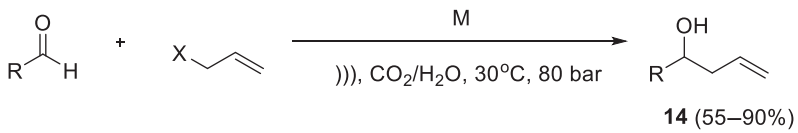
It was reported [32] that aldehydes under sonication in the ultrasonic cleaning bath (50 kHz) reacted with the mixture of magnesium and 6-bromo-1-butene in THF to afford secondary alcohols, for example, **13** (Scheme 9). It should be noted that 1,2-dibromoethane was used in the reaction as an activator. Being rather general, the reaction was effectively applied to a variety of aliphatic, aromatic, and heteroaromatic aldehydes to provide the corresponding alcohols (12 examples, 52%–96% yields). Hexanal in this



Scheme 9 Ultrasound-assisted synthesis of 1-phenylpent-4-en-1-ol (**13**).

reaction gave the lowest yield (52%) that was attributed to volatility of the substrate. A relatively low yield (57%) of the product of the addition to thiophenyl aldehyde was explained by its partial decomposition under the reaction conditions.

Similar to magnesium, other metals were also reported [33] to facilitate addition to aldehydes in their reaction with alkylhalides under sonication. This variation of the Zaitsev reaction of aldehydes with allyl halides in the presence of zinc and tin was performed in the subcritical (30°C, 80 bar) CO_2/H_2O mixture as a solvent (Scheme 10). The application of CO_2 as a medium for the reaction improved solubility of organic reagents in the reaction media and allowed convenient isolation of allylation products **14**. It was also reported [33] that yields and selectivity of the reaction toward homoallylic alcohol could



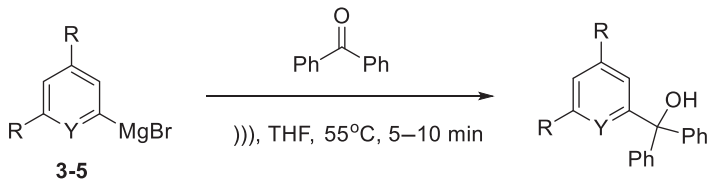
R = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *o*-ClC_6H_4, (*E*)-PhCH=CH;
X = Cl, Br;
M = Zn, Sn

Scheme 10 Ultrasound-supported organometallic reaction of aldehydes in the subcritical CO_2/H_2O media.

be improved by higher temperature, addition of sodium or ammonia chlorides, and Tween 80 as a surfactant stabilizing the emulsion, which was formed under sonication of the CO_2/H_2O biphasic reaction mixture.

2.2.2 Reaction of Grignard reagents with ketones

The Grignard reagents **3**–**5** prepared using the sonication protocol (Scheme 3) were further reacted in a one-pot manner with benzophenone under ultrasound irradiation to afford the corresponding tertiary alcohols **15**–**17** in good yields (Scheme 11) [26]. The same cup horn (300 kHz, 200 W) was used in this second step of the process. It should be noted that 2-pyridylmagnesium chloride (**6**) reacted identically to its bromide

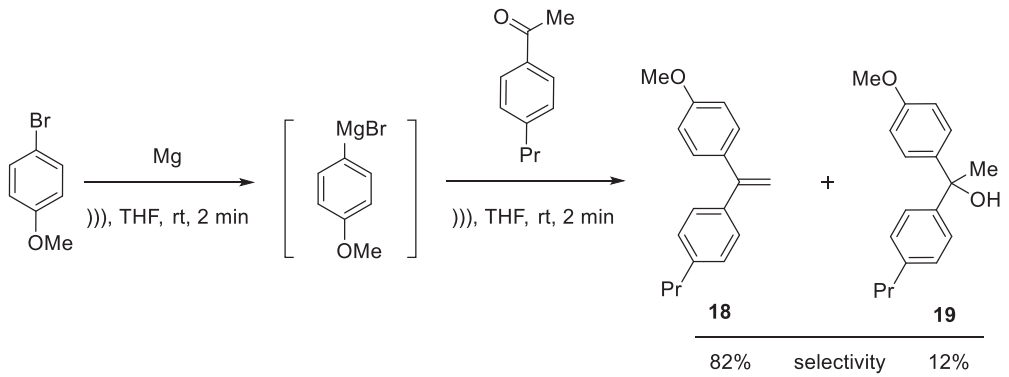


Y = CH, R = H, **15** (98%); OMe, **16** (84%);
Y = N, R = H, **17** (94%)

Scheme 11 Ultrasound-assisted reaction of benzophenone and Grignard reagents **3**–**5**.

analog **5**. The method conveniently combined the synthesis of Grignard reagents from poorly reactive (het)aryl halides and the subsequent reaction of the Grignard reagents, as sonochemical transformations.

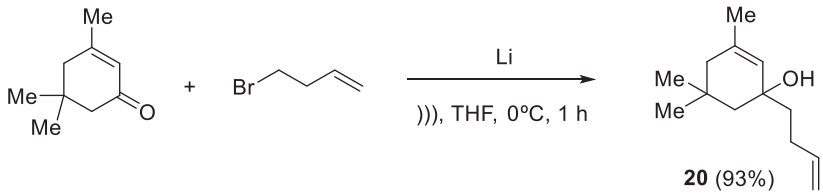
The sonication protocol was applied to both steps, the formation of arylmagnesium bromides and their reaction with acetophenones [34]. It was demonstrated that ultrasound irradiation effectively promoted the reaction without prior drying of solvent and requirements of inert atmosphere. The first step of the Grignard reagent formation proceeded smoothly. However, in the second step the authors observed two main products generated in different proportions. The reaction of 4-methoxyphenylmagnesium bromide, prepared in the first step from *p*-bromoanisole and magnesium, with 4-propylacetophenone resulted in the formation of the addition product **19** together



Scheme 12 Synthesis of 4-methoxyphenylmagnesium bromide and its reaction with 4-propylacetophenone under ultrasound irradiation.

with the product of dehydration **18** as the major component (Scheme 12). The conversion of 4-propylacetophenone in this reaction was 92%. The selectivity of the process was found to depend greatly on the reaction time and structure of substrates.

Grignard reagents are often not very effective and selective as building blocks in sonochemical additions to ketones. For example, Grignard reagent derived from 4-bromo-1-butene did not afford appreciable quantity of alcohol **20** in the reaction with isophorone. Instead, a mixture of **20** with the elimination and 1,4-addition products was

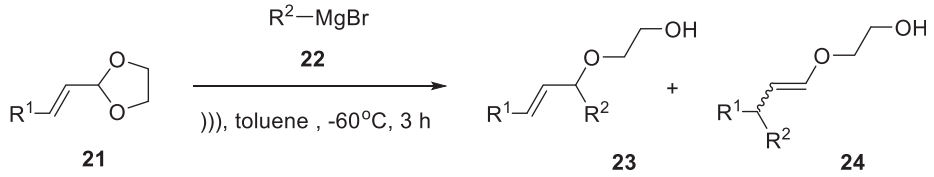


Scheme 13 Ultrasound-assisted synthesis of tertiary alcohol **20**.

formed [35]. The selectivity of the process was improved when lithium was used instead of magnesium in the Barbier-type reaction under ultrasound affording the desired 1,2-addition product **20** in good yield (Scheme 13).

2.2.3 Reaction of Grignard reagents with acetals

The effect of ultrasound irradiation on the addition of Grignard reagents **22** to masked aldehydes, that is, acetals of α, β-unsaturated aldehydes **21** was explored [36]. It was found that sonochemical protocol under low temperature (−60°C) and ultrasonic irradiation (50 W) enhanced the addition of Grignard reagents **22** to acetals **21** without affecting the selectivity of the reaction (Scheme 14). The yields under silent conditions were 4%–63%, while under sonication they were above 62% and nearly quantitative for most of the substrates. The 1,2-addition products **23** were predominant (sometimes exclusive)



R^1=Me, *n*-Pr, Ph

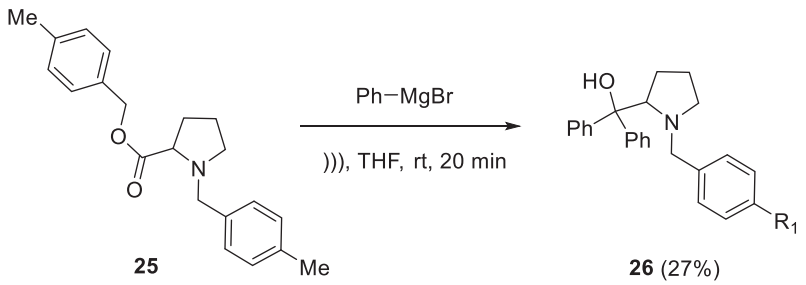
R^2=Me, Et, *n*-C_4H_{10}, Ph, $CH_2CH{=}CH_2$

Scheme 14 Ultrasound-assisted reaction of acetals **21** with Grignard reagents **22**.

in the reactions. Only small quantities of geometrical isomers **24** as the products of 1,4-addition were detected for some substrates.

2.2.4 Reaction of Grignard reagents with esters

The ultrasound irradiation was applied to facilitate the reaction of proline ester **25** and its analogs with arylmagnesium bromides [37]. For example, in the reaction of **25** with



25 **26** (27%)

Scheme 15 Reaction of proline ester **25** with phenylmagnesium bromide.

phenylmagnesium bromide, compound **26**, possessing potent insecticidal activity against aphids, was obtained (Scheme 15). A few insecticidal compounds were prepared using this method.

3. Concluding remarks

Sonication has been demonstrated to promote the formation of Grignard reagents facilitating the reaction of alkyl, aryl, and hetaryl halides with magnesium. Compared to conventional synthesis, this process under ultrasound irradiation was found to be less demanding to solvents and more efficient in the conversion of the original halides into the corresponding organomagnesium halides. It was also demonstrated that sonication accelerated the formation of Grignard reagents and improved selectivity of the reactions often making practical the one-pot Barbier-type reaction of magnesium, halides, and carbonyl compounds without prior preparation of Grignard reagents. The reactions of Grignard reagents with carbonyl compounds under sonication in many cases resulted in a better outcome compared to conventional conditions. However, occasionally sonication protocols for the Grignard reaction gave unexpected results, such as the formation of products different from those obtained from synthetic procedures utilizing conventional conditions. Additional experiments are required to understand the role of ultrasound in the facilitation of the Grignard reaction.

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CHAPTER 10

Sonochemical approach for the synthesis of organo-modified layered double hydroxides and their applications

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1. Introduction

Among different methods of carrying out organic synthesis such as photochemistry, microwave-assisted chemistry, wet chemistry, hydrothermal approach, flame pyrolysis, and sonochemistry, the latter has been proposed as an economical method in terms of time and cost and is based on chemical activation [1]. Ultrasonic waves are used in various fields of chemistry including synthesis, destroying both biological and chemical pollutants from the environment, etc. Also, they can be used for improving procedures related to the polymer chemistry and engineering areas, e.g., extraction, crystallization, and electroplating [2]. For example, in the process of producing biodiesel from blended oil feedstock, applying the ultrasound in comparison to the mechanical mixing showed a higher yield of the transesterification [3]. In another study [4], using sonochemistry in the emulsion polymerization of methyl methacrylate and preparation of its nanocomposites led to an enhancement in the final conversion.

The first usage of ultrasonic waves in chemistry dates back to 1927 by Richards and Loomis [5]. They acclaimed that the compressional waves with high frequency can accelerate certain chemical reactions. From those times to now the ultrasonic technology has been used in a broad range of synthetic reactions mainly the synthesis of nanomaterials, including metal oxides, alloys, semiconductors, as well as carbonic and polymeric materials and their nanocomposites because it generally meets the goals of the green chemistry [6, 7]. In recent years, it has been introduced as a green and environmentally benign technique for the surface modification of the nanoparticles with different types of molecules and preparation of polymer-based nanocomposites. It induces surface activation, deagglomeration, and proper dispersion of the nanofillers within the polymeric phase [8]. On the other hand, it can be a proper source of energy to induce the reaction between nanoparticles and organic counterpart [9]. These demands are met by neither mechanical

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nor magnetic stirring [8]. The efficiency of this technique is as a result of two phenomena, i.e., acoustic cavitation and acoustic streaming [10]. Fig. 1 shows a statistical comparison of using sonochemical in the field of nanoparticles surface modification during several years and confirmed that a new era has been introduced in this domain.

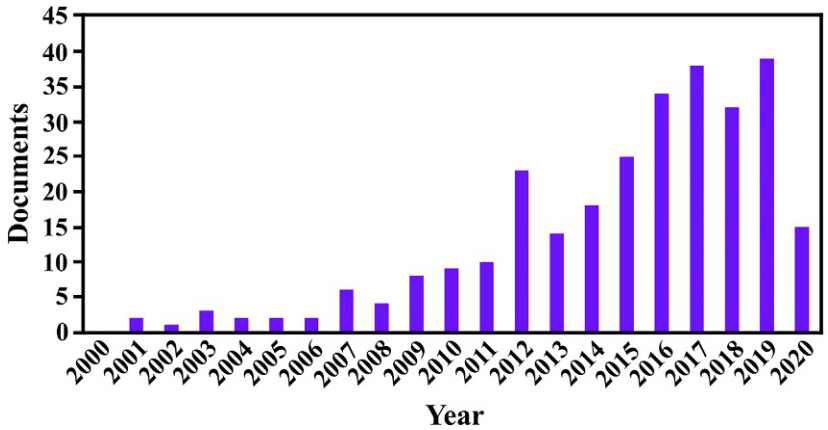

Fig. 1 Search results from the Scopus website for the number of documents per year with the keyword of "surface modification of nanoparticles using ultrasound" including article titles, abstract, and keywords (obtained on April 2020).

In this chapter, we will concentrate specifically on the role of ultrasound waves in the synthesis of organo-modified/layered double hydroxide (LDH)s and their nanocomposites with different applications.

2. A summary on the ultrasonic approach

2.1 Transducers configuration

The sonochemical instruments are typically available as ultrasonic horns, baths, and cup-horn devices of which the latter is a midway of a horn and bath instrument [11]. To direct sonication, the ultrasonic horn can be used, though two others are applied for indirect irradiation. The frequency range applied in horn case starts from 20 to 50 kHz, while higher frequencies are accessible by ultrasonic baths [1]. Rahimi et al. [12] found that compared to the ultrasonic bath, horn systems induce higher ultrasonic intensity into the liquid media. Mohod et al. [13] observed that using an ultrasonic horn instead of a bath leads to more local cavitational activity and greater extent of energy scattering within the liquid media. Although the lack of a mixing system limits their applications, the ultrasonic baths are simple and cost-effective and can be scaled up for industrial purposes [14]. The most important point, which is usually ignored in using an ultrasonic horn, is calibrating the ultrasonic output to report the exact experimental conditions.

This can be done by calorimetry. Ultrasonic baths can be good alternatives, which have a lower power density compared to a horn. Despite ultrasonic horns, which have chemical outcomes, ultrasonic baths cover physical aspects. For instance, they can be used for activation of highly reactive metals, easy solvation of solids or crystallization, and exfoliation of layered materials [15]. Consequently, by taking into account our expectations and experimental conditions, we can choose a proper device. For example, in the synthesis of nanomaterials applying different types of irradiation system leads to different morphologies for the resulted materials. In this regard, Sharifalhoseini et al. [11] investigated the effect of sonication type on the morphology of the synthesized ZnO nanostructure. As can be seen from Fig. 2, using three different irradiation systems meaning a horn equipped, an ultrasonic bath, and a cup-horn system led to different morphologies including rod-shaped, flower-like, and network for the nanostructures, respectively.

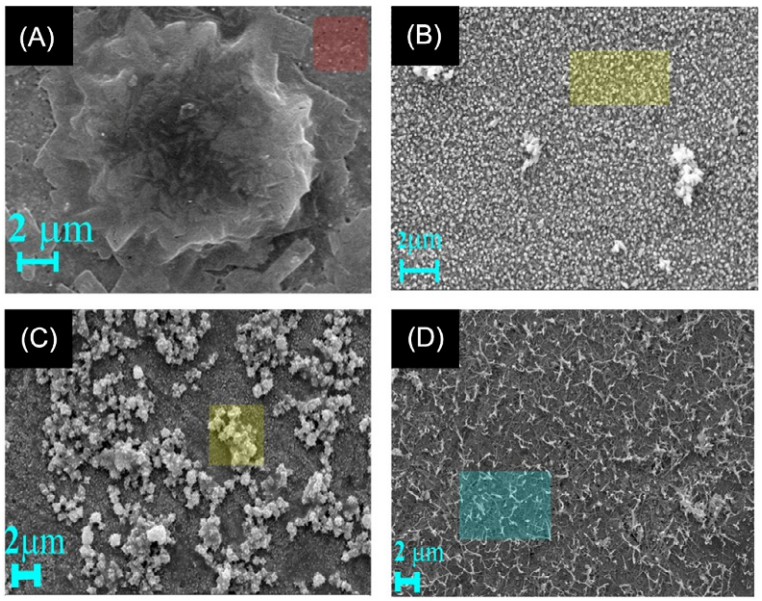

Fig. 2 (A) The micro-sized spherical structures and the zinc oxide nanostructures could be observed, (B) zinc oxide nanorods with uniform distribution on the surface of the product prepared by direct sonication, (C) surface morphology of sample prepared by ultrasonic bath, and (D) SEM micrographs of the sample prepared by ultrasonic cup horn. *SEM*, scanning electron microscopy. *Adopted from Z. Sharifalhoseini, M.H. Entezari, M. Shahidi, Sonication affects the quantity and the morphology of ZnO nanostructures synthesized on the mild steel and changes the corrosion protection of the surface, Ultrason. Sonochem. 41 (2018) 492–502, with kind permission of Elsevier.*

In a study by Thompson et al. [16], the effect of the type of sonication (direct or indirect) on the properties of a series of zeolitic imidazolate framework (ZIF-8)/Matrimid composite membranes was investigated. The composites prepared by direct sonication (applying a sonication horn) showed better dispersity for the ZIF-8 within the polymeric

matrix. Also, the mentioned composites showed better CO_2 permeability and CO_2/CH_4 selectivity compared to those prepared via indirect irradiation (applying a sonication bath).

2.2 Mechanism

The ultrasound frequency ranges from 20 kHz to 100 MHz, while the conventional sonochemistry lies between 20 and 40 kHz [2]. The exact mechanism of the sonochemical process is based on the acoustic cavitation phenomenon. In fact, when sound waves pass through a reaction mixture, induce dynamic tensile stress, which leads to the creation of bubbles. These bubbles grow to a critical size and then collapse [15]. It is an adiabatic process, in which releasing a high amount of energy creates hot spots with a temperature of about 5000°C and pressure of 2000 atm (Fig. 3) [17].

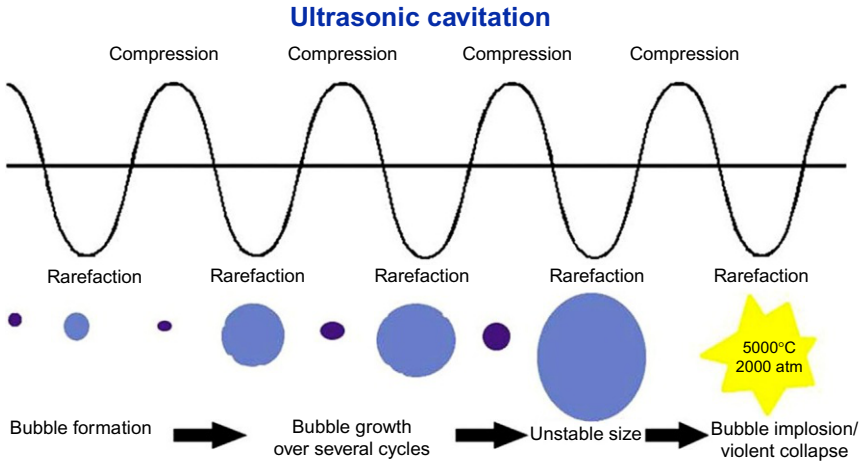

Fig. 3 Schematic representation showing the mechanism of acoustic cavitation which is used in the sonochemical processing method. *Adopted from A. Moghtada, R. Ashiri, Superiority of sonochemical processing method for the synthesis of barium titanate nanocrystals in contrast to the mechanochemical approach, Ultrason. Sonochem. 41 (2018) 127–133, with kind permission of Elsevier.*

This phenomenon justifies the role of ultrasonic waves in enhancing the rate of reactions and improving the dispersion of nanoparticles in a media, e.g., a polymeric matrix in the process of nanocomposite synthesis [18]. Compared to other sources of energy used in the chemical synthesis like heat and light, the ultrasound creates a million zones with more concentrated energy content within the liquid. Under these circumstances, the vaporized molecules of the reaction mixture inside the cavitating bubbles can be destroyed and could cause the formation of free radicals as well. These reactive species can promote further oxidation and reduction in the reaction medium. These conditions

also induce interparticle collisions between the particles and consequently propose a solution for the agglomeration issue [19].

3. Synthesis of organo-modified/LDHs and their nanocomposites with prospect applications

LDHs are a group of ionic compounds with the brucite-like structure in which cationic hydroxide sheets are close together via interacting with interlayer anions. Their general formula is $[M^{2+}_{1-\chi}M^{3+}_{\chi}(OH^{-})_2]^{\chi+}(A^{n-})_{\chi/n}\cdot mH_2O$ in which M^{2+}, M^{3+}, and A^{n-} are representative of di- and trivalent metal cation, and an exchangeable hydrated anion, respectively [20]. They have vast applications in catalysts [21], sensors [22], and electrodes [23], as well as drug delivery systems [24]. Recently, LDH nanostructures and their nanocomposites have attracted a lot of attention in the field of wastewater treatment [25].

Modification of LDH is crucial especially from the perspective of nanocomposites preparation. During modification, intercalation of LDH with different organic moieties leads to expanding the interlayer space of the LDH and consequently better intercalation of a large hydrophobic polymeric chain. Meanwhile, surface modification of LDH endues it with organophilic character [26].

A large number of compounds have been applied for the modification of the LDH and preparation of the nanocomposites. Herein, organic compounds as a huge class of modifiers are more attractive, since they provide characteristics, which are rather more favorable than the others. Dyes, drugs, vitamins, polymers, and different allotropes of carbon, including carbon black, carbon nanotubes (CNTs), and graphene oxide (GO) are some members of this group.

Hitherto, several strategies have been proposed to prepare organo-modified LDH structures, i.e., coprecipitation, anion exchange, and reconstruction. In the first approach, the LDH layers are fabricated in the related metal ion salt solutions and the presence of an organic moiety. In the anion exchange protocol, the interlayer anion of the LDH is replaced by an anionic organic molecule. This method has some difficulties in the term of industrialization since in some cases the interlayer anions are more prone to be bonded with layers (e.g., CO_3^{2-}). Temperatures over 450°C can disturb the lamellar structure of the LDH. In the presence of water and anionic organic molecules and during the reconstruction path they can reassemble and create the original structure of LDH [27]. In this chapter, we will focus on those approaches conducted sonochemically for the organic modification of LDH structures and discuss their numerous applications in different fields. As mentioned before, the ultrasonic irradiation is an appropriate tool to prepare nanoparticles, which are organically modified. Since it can break hydrogen bondings among them and separate their aggregates. After irradiation of nanoparticles, the number of accessible hydroxyl groups on their surface will increase [28]. Under this circumstance, the interaction of the nanoparticles with several organic modifying agents will be improved [29]. Also, the organic phase can be dispersed in the reaction mixture properly.

3.1 Carbon derivative/LDH structures

Nowadays, carbon-based nanoparticles have been introduced to the world as six main groups, i.e., graphene compounds, CNTs, mesoporous carbons, nanodiamonds, fullerenes, and carbon dots [30]. Their combination with LDHs to prepare organic/LDH nanocomposites has attracted much more attention in recent years.

Zhao et al. [31], ultrasonically dispersed GO in deionized water and then prepared a GO/LDH nanostructure during a hydrothermal process. The results of the X-ray photoelectron spectroscopy demonstrated an enhancement for the carbon signal of the carboxylate functional group, which could be as a result of intercalated CO_3^{2-} in the LDH structure. They acclaimed that the resulted nanohybrid can be applied as a thermal or electrical conductive as well as a flame-retardant material.

Xia et al. [32] used an ultrasonic bath to exfoliate GO and then it was reduced via a hydrothermal route. After ultrasonic (bath)-assisted dispersion of the reduced GO (RGO) in *N,N*-dimethylformamide, related salts of the LDH were added. As can be seen from transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images in Fig. 4, two amounts for interlayer spacing are noticeable (0.25 and 0.32 nm) in which the first relates to the (012) plane of LDH with hexagonal morphology and the second corresponds to (002) crystallographic planes of graphitic carbon. These confirm the synthesis of the RGO/LDH moiety with proper contribution of both counterparts in its structure. The results showed that the RGO/LDH structure has the potential use as an electrocatalyst since it showed high oxygen evolution reaction activity with a low overpotential of 250 mV.

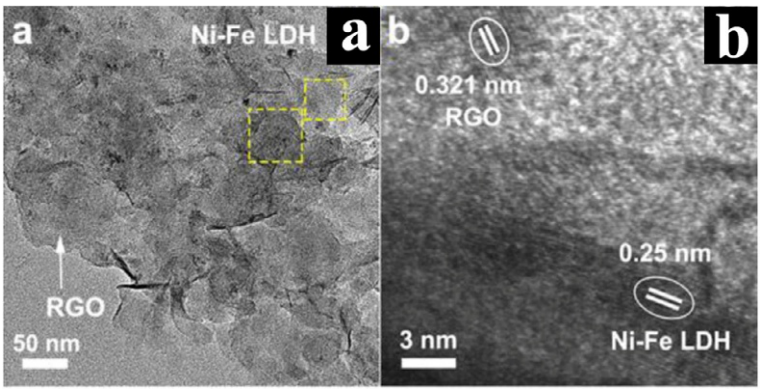

Fig. 4 (A) TEM and (B) HRTEM images of the RGO-Ni-Fe LDH composite. *TEM*, transmission electron microscopy; *HRTEM*, high resolution TEM; *RGO*, reduced graphene oxide. *Adopted from D.-C. Xia, L. Zhou, S. Qiao, Y. Zhang, D. Tang, J. Liu, H. Huang, Y. Liu, Z. Kang, Graphene/Ni–Fe layered double-hydroxide composite as highly active electrocatalyst for water oxidation, Mater. Res. Bull. 74 (2016) 441–446, with kind permission of Elsevier.*

Yuan et al. [33], made the GO exfoliated using sonication for 1 h. After addition of the related metal salts of the LDH to the above suspension, it was further sonicated for 30 min to make it ready for a hydrothermal process. The resultant material showed good performance in the removal of Cr^{6+} from aqueous solutions, which could be as a result of good dispersion and synergism among two counterparts of the nanocomposite.

GO/LDH nanocomposites with the ability of SeO_4^{2-} and Sr^{2+} uptake from radioactive wastewater were synthesized using sonication [34]. For this purpose, suspensions of GO with different weight percentages were prepared using ultrasonic irradiation at 28 kHz for 3 h and after mixing with LDH, nanocomposites were attained during a freeze-drying process. The results of powder X-ray diffraction (XRD) of the nanocomposites showed a decrease in d_{003} spacing with increasing the GO content. They explained that enhancing the partial NO_3^- releasing as a result of partial charge neutralization by the GO's functional groups may be responsible for this occurrence.

Youn et al. [35] used the ultrasonic tool in the process of the preparation of the RGO/LDH composite to disperse GO in water. The resulted nanocomposite can play the role of an electrocatalyst in the electrochemical and photoelectrochemical water oxidation. For this aim, it was dispersed ultrasonically in the ethanol and the resulted solution was deposited on to the hematite photoanode, which was used as the working electrode. It was observed that the photocurrent of the hematite photoanode was improved by two times, while the onset potential was shifted negatively.

Fang et al. [36] reported the synthesis of aerogels based on GO contained LDH. They mentioned that sonication of the mixture for 1 h changed its color from original brown to a darker brown. Interactions including charge-assisted hydrogen bonds and lattice-lattice cation-π among the GO and LDH are responsible for this observation. Hence, the resulted aerogels showed excellent structural stability and hydrophilicity and were used successfully for the uptake of methylene blue (MB) and Cd^{2+} from wastewater.

In the procedure of CNT/LDH nanohybrids synthesis, use of ultrasonication has been reported to gain good dispersion of CNT before use [37]. As demonstrated in Fig. 5, CNT underwent acid treatment and then sonication to disperse in alkaline solution. Next, the adsorption of metal ions occurred and LDH sheets were shaped by nucleation and growth during a hydrothermal process. The resulted CNT/LDH nanocomposite with amphiphilic characteristic was able to play the role of an emulsifier at the water-oil interface. Finally, it was used as catalyst support and showed high catalytic activity for the selective oxidation of benzyl alcohol to benzaldehyde. The conversion was 92% for the reaction time of 5 h.

In an experiment by Khodam et al. [38] ultrasonication was used for both surface modification of CNTs and synthesis of CNT/LDH nanohybrids. In this regard, CNT was first sonicated for 20 min and then underwent oxidation. After treating the CNT in NaOH to gain negative charge, it was dispersed in deionized water using

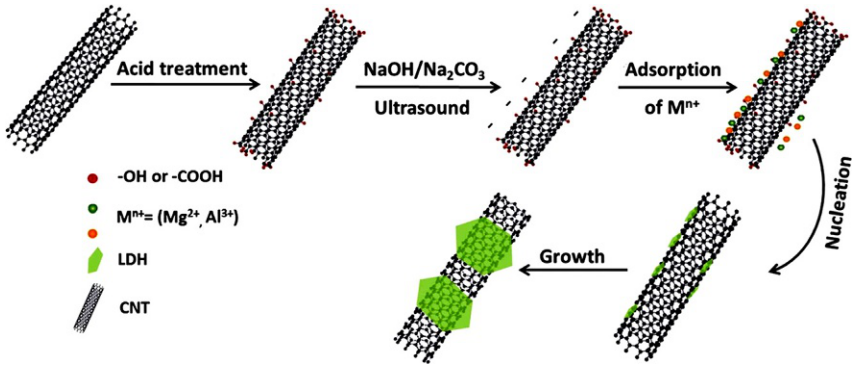

Fig. 5 Schematic of the synthetic process and formation mechanism for the LDH-CNT nanohybrids. *CNT*, carbon nanotubes. *Adopted from Y. Shan, C. Yu, J. Yang, Q. Dong, X. Fan, J. Qiu, Thermodynamically stable pickering emulsion configured with carbon-nanotube-bridged nanosheet-shaped layered double hydroxide for selective oxidation of benzyl alcohol, ACS Appl. Mater. Interfaces 7 (2015) 12203–12309, with kind permission of American Chemical Society.*

ultrasonication. Next, the synthesis of LDH was performed in the presence of the CNT during a coprecipitation method. Brunauer-Emmett-Teller (BET) measurements confirmed higher surface area of the resulted nanohybrid than the neat LDH. The fabricated nanohybrid demonstrated high efficiency in the removal of Acid Red 14.

Yang et al. [39] prepared CNT/LDH composites with good electrochemical performance. For this purpose, before synthesis they first oxidized the surface of the CNT via sonication for 6 h in the presence of a mixed solvent including nitric acid and sulfuric acid. They confirmed successful fabrication of this composite via comparison of its TEM images with the composite prepared via physical mixing of the LDH and CNT. Thus, the role of sonication in the pretreatment of CNT for the fabrication of the composites could be imperative. Also, the electrochemical properties of the CNT/LDH composite were studied and they understood that it has satisfactory electrochemical characteristics, e.g., increasing average discharge capacity, high cycle stability, lower charge plateau voltage, as well as higher discharge plateau voltage. Therefore, the resulted composite can be a good candidate to be used as the anode material in Ni-Zn cells. In several other studies [40–44], sonication was used for the preparation of CNT/LDH nanohybrids.

In an experiment performed by Xie et al. [45], ultrasonic irradiation was used for the treatment of magnetic carbon spheres. Then, the LDH prepared by coprecipitation method was loaded with these magnetic carbon spheres. The scanning electron microscopy (SEM) image of the prepared composite revealed stacked layers of the LDH with

small plate-shaped units. The composites were used for the elimination of the Cu^{2+} and Pb^{2+} from wastewater.

In the study by Zhang et al. [46], the pretreatment of a glucose solution before subjecting to the hydrothermal process was done by sonication. In this regard, Fe_3O_4 microspheres were firstly dispersed in HNO_3 via sonication for 10 min and then dispersed in the solution of glucose using ultrasound irradiation for 5 min. The resulted carbon-coated Fe_3O_4 structure was then used for the LDH nanosheets to grow on it. The fabricated Fe_3O_4/carbon/LDH nanostructure showed the adsorption capacity of 174 mg/g for U^{6+}. That is because of the enhancing of functional groups after coating LDH with a carbon layer. They mentioned two probable mechanisms for the adsorption, i.e., surface adsorption or intercalation mechanism.

LDH was coated on a porous carbon structure obtained from biomass using an ultrasound-assisted method [47]. In this regard, different amounts of LDH and porous carbon were dispersed during sonication before carrying out the hydrothermal process. The composite with 13.8% mass ratio of LDH had the highest efficiency for the removing of Cr^{6+} and methyl orange (MO) at the same time. This observation was in agreement with BET data, which showed the highest surface area (1273 m^2/g) for the nanocomposite with a mass ratio of 13.8%.

Yu et al. [48] prepared a series of LDH composites coupled with different kinds of nanostructured carbon compounds. For this aim, they first dispersed carbon species including carbon black, CNT, GO, and CNT/RGO using sonication for 30 min, separately. It was demonstrated that the CNT/RGO/LDH composite has better performance as a pseudocapacitor. Therefore, it can be a good alternative electrode in different kinds of lithium batteries and solar cells.

3.2 Drug/LDH structures

Different kinds of drugs hitherto have been used for the insertion within the LDH layers with the aid of sonication. For example, hybrid films of GO/drug intercalated LDH were prepared through an ultrasonic method [49]. At first, GO was suspended in water using sonication for 2 h. Afterward, LDH was intercalated with benzylpenicillin (BP) potassium salt during ion-exchange. The resulted BP/LDH was suspended in water using sonication for 2 h. Finally, two suspensions were mixed under stirring and then sonication for 2 h. The mass ratio of BP/LDH was varied in the resulted films. By decreasing the GO content the release time was enhanced. Also, the nanocomposite films presented antibacterial activity, which arose from both GO and BP.

Kamyar et al. [50] prepared a type of LDH nanohybrids intercalated with dexamethasone (DEXA) through an ion-exchange process. For this aim, they first dispersed DEXA phosphate in deionized water using ultrasonic irradiation. After preparation of

the nanocomposite, it was deposited on the anodized titanium. In vitro release tests showed that the resulted material has the potential to be used for bone implant applications.

In another study [51], the LDH was intercalated with methotrexatum (MTX) as an antifolate drug. At the first stage to attain positively charged sheets, LDH was delaminated in formamide through sonication and then reassembled in the presence of dissolved MTX anions. A translucent suspension of LDH was attained using sonication and it showed a Tyndall effect. As this suspension was added to the solution of the MTX and due to its insertion within the LDH intergalleries, this effect was not observed at all. As can be seen from photographs (Fig. 6), the appearance of the suspension of the LDH in formamide was changed from a clear steady state to a turbid viscous state, which shows the effect of sonication on the exfoliation of the LDH. The resulted MTX/LDH hybrids showed an inhibitory effect on the development of cancer cells.

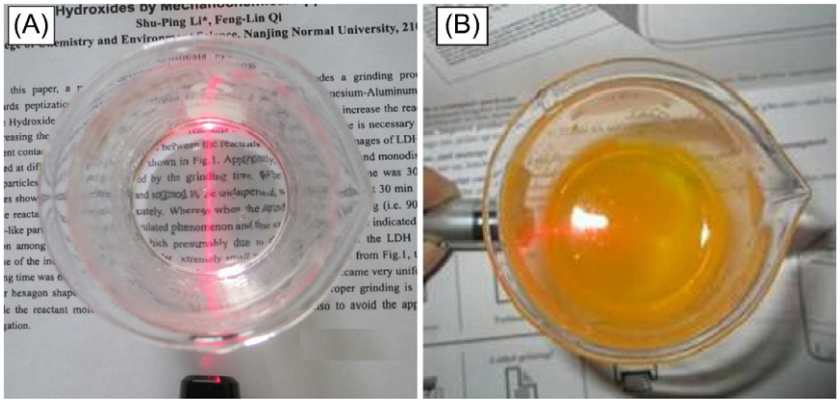

Fig. 6 Photographs of (A) colloidal suspensions of the exfoliated LDHs and (B) the suspension containing LDHs and MTX. *MTX*, methotrexatum. *Adopted from S.-Q. Liu, S.-P. Li, X.-D. Li, Intercalation of methotrexatum into layered double hydroxides via exfoliation-reassembly process, Appl. Surf. Sci. 330 (2015) 253–261, with kind permission of Elsevier.*

Ultrasonic treatment was carried out in several steps of the synthesis of nanovehicles consisting of LDH intercalated with Fluorouracil (5FU) as an anticancer drug [52]. The procedure for this synthesis is as follows: first, Y_2O_3:Er^{3+},Yb^{3+}@SiO_2 nanoparticles with negative surface charge were prepared using sonication. Afterward, a layer of LDH was formed on them and the 5FU was inserted within the LDH layers during an ultrasonic-assisted route. The resulted system has the potential to be used for the optical tumor imaging as well as therapy, at the same time.

3.3 Polymer/LDH structures

Recently, polymer/LDH composites have become an important field of research. The outcomes of interactions among LDH and polymers can be classified into three different categories. In some cases, they are phase-separated. The LDH also can be intercalated with polymers and even exfoliation of the LDH can occur [53]. The resulted composites have outstanding properties provided fine dispersion of the LDH within the matrix and good binding among them.

In a study done by Lyu et al. [54], an emulsion-cross-linking technique was used to synthesize a chitosan (CS)/LDH nanocomposite. In this strategy, ultrasonic waves were applied to disperse CS and LDH in a solution of acetic acid, separately. After mixing and cross-linking in the presence of the epoxy chloropropane, the prepared nanocomposite showed good adsorption of Pb^{2+} and Cd^{2+} from contaminated water. The adsorption process obeyed Langmuir and pseudo-second-order for the isotherm and kinetic models, respectively.

In the work of Hajibeygi et al. [55] ultrasonic irradiation was used for the preparation of the poly(amide-imide) (PAI)/LDH nanocomposites. In this regards, first of all organically modified LDH was prepared using two types of the modifiers including diacid-diimide and sodium dodecylbenzene sulfonate. Then, a distinctive amount of the organically modified LDH was added to PAI solution. The resulted mixture was subjected to high-intensity ultrasonic irradiation for 45 min before casting. Thermal characteristics of the polymer were improved after the addition of the organically modified LDH.

Mallakpour et al. [56], intercalated LDH with *N,N′*-(Pyromellitoyl)-bis-L-methionine as a type of a diacid using 1 h sonication. The organo-modified LDH was then entered to the PAI matrix at three different weight percentages to prepare nanocomposites under sonication for 2 h. The TEM results showed that the morphology and particle size of the organically modified LDH was changed after insertion into the PAI matrix. Since under sonication, the number of the polymer chains entered the interlayer of organically modified LDH were enhanced and delamination and exfoliation of the LDH occurred faster.

Mallakpour et al. [57], synthesized folic acid (FA) intercalated LDH and then added it to the CS matrix with different weight percentages. Both of these steps were accomplished using sonication. The in vitro release of FA was scanned at simulated conditions of the gastrointestinal tract. They acclaimed that by using sonication, homogenous dispersion of the nanofiller in the CS matrix will be attained. It can be seen from field emission scanning electron microscopy (FE-SEM) images in Fig. 7, the morphology of the FA/LDH has changed after adding to the CS matrix and a porous structure is observable in the case of polymer nanocomposite. The results showed that compared to FA/LDH, controlled release of the drug occurred from CS/FA/LDH nanocomposite at similar conditions to stomach after 8 h. So, the presence of CS can modify the behavior of FA/LDH for drug delivery purposes.

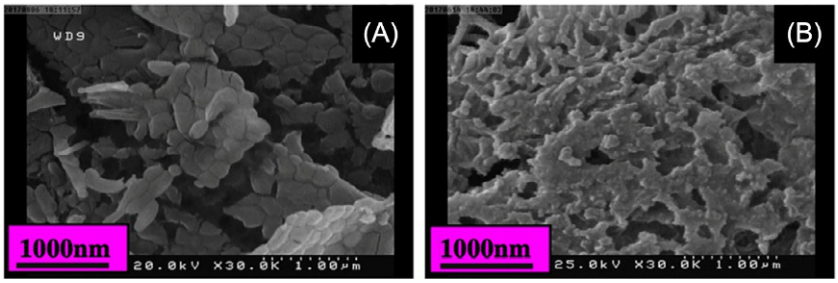

Fig. 7 FE-SEM images of (A) LDH-FA and (B) LDH-FA/Cs. *FE-SEM*, field emission scanning electron microscopy. *Adopted from S. Mallakpour, M. Hatami, Fabrication and characterization of pH-sensitive bio-nanocomposite beads havening folic acid intercalated LDH and chitosan: drug release and mechanism evaluation, Int. J. Biol. Macromol. 122 (2019) 157–167, with kind permission of Elsevier.*

Zubair et al. [58] synthesized a series of composites containing LDH and different portions of starch. Sonication (5 min) was used for dissolving starch in deionized water. The starch/LDH composites were used for the removal of the MO from aqueous solution. Based on the reported maximum adsorption capacity of 246.91, 358.42.91, and 387.59 mg/g for bare LDH, starch/LDH (2:1), and starch/LDH (1:1) composites, the resulted composites had high efficiency in the dye removal.

Mallakpour et al. [59] also applied ultrasonic irradiation in both steps of the organic modification of LDH and fabrication of its composites with PAI. First of all, LDH was intercalated with *N,N′*-(pyromellitoyl)-bis-L-phenylalanine under ultrasonic irradiation. Then, PAI was dispersed in absolute ethanol by sonication for 30 min. After mixing the resulted colloid with desired amounts of modified LDH, it was further sonicated for 1 h. The results of the thermogravimetric analysis (TGA) showed that degradation of the nanocomposites occurred at higher temperatures compared to the neat polymer and it moved to higher temperatures with increasing the modified LDH content.

Huang et al. [60] synthesized a series of polyamide 6 (PA6)/CNT/LDH hybrid nanocomposites using an ultrasonic route. Specific amounts of CNT/LDH hybrid and ε-caprolactam were added to a flask and the resultant was sonicated for 60 min at 80°C. Then, they were fabricated after adding 6-aminocaproic acid. The stress-strain curves of the nanocomposites and pure PA6 are shown in Table 1. It is obvious that mechanical strength has increased with the incorporation of the CNT/LDH hybrids. In fact, a synergism between LDH and CNT and also proper dispersion of its hybrid in the matrix of polymer leads to stress transfer from PA6 to the CNT/LDH hybrid.

Table 1 Summary of mechanical properties of neat PA6 and its nanocomposites.

Sample	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Neat PA6	1.0 ± 0.1	55.0 ± 0.3	220.0 ± 33.6
PA6/LDH (1.0 wt%)	2.0 ± 0.1	62.1 ± 0.2	74.8 ± 12.5
PA6/CNT (1.0 wt%)	2.5 ± 0.1	63.9 ± 0.1	102.3 ± 22.5
PA6/Hybrid (2.0 wt%)	3.1 ± 0.1	74.3 ± 0.5	41.5 ± 5.6

Adopted from S. Huang, H. Peng, W.W. Tjiu, Z. Yang, H. Zhu, T. Tang, T. Liu, Assembling exfoliated layered double hydroxide (LDH) nanosheet/carbon nanotube (CNT) hybrids via electrostatic force and fabricating nylon nanocomposites, J. Phys. Chem. B 114 (2010) 16766–16772, with kind permission of American Chemical Society.

Ultrasonication has been used in both synthesis process of RGO/LDH as well as poly(methyl methacrylate) (PMMA) based composites [61]. They mentioned that a uniform suspension of RGO/LDH in the $CHCl_3$ was prepared using an ultrasonic bath. Then, they added the resulted RGO/LDH hybrid to PMMA to enhance its thermal resistance. Again a synergism between catalytic carbonization of the LDH and physical barrier of the RGO is responsible for this observation.

Zhao et al. [62] used sonication for the preparation of the polyimide (PI) film containing CNT/LDH. For this aim, at first a hierarchical nanocomposite of CNT/LDH was prepared. The resultant was dispersed in dimethyl acetamide using an ultrasonic bath for 3 h at room temperature in the presence of 4,4′-diaminodiphenyl ether. After dissolving of pyromellitic dianhydride in this suspension, it was transferred into glass slides. By using a film-coating device, the desired thickness for the film was attained. The results of the tensile test showed advancement in mechanical features, including tensile modulus (MPa), tensile strength (MPa), elongation at break (%), and energy absorbed (kJ/kg). By taking account of these features, the mentioned protocol can be applied in the design of novel structures with applications in catalysts, ion transportation, energy conversion, etc.

Perreira et al. [63] improved dispersity of LDH by using the ultrasonic treatment for 5 min before reversible addition-fragmentation chain transfer (RAFT)-assisted encapsulating emulsion polymerization (REEP), which was a process for the waterborne polymer encapsulation of the LDH. They pointed out that the obtained nanocomposites have the potential to be used in coatings and adhesives technologies.

In a study [64], sonication was used for the preparation of a series of PI nanocomposites filled with CNT/LDH. At first, CNT was dispersed in an alkaline solution using a sonication bath (30 min irradiation). Then, the CNT/LDH was prepared by irradiation of the CNT suspension in the presence of the metal salts of the LDH for 1 h. After preparation of the CNT/LDH, the uniform colloidal dispersion of the PAI

was obtained by subjecting it to irradiation for 15 min. Finally, different concentrations of the CNT/LDH were added to it and then it was sonicated for 1 h. The resulted nanocomposites showed enhancement in onset degradation temperature and char yield (remaining mass at 800°C) values.

Zhou et al. [65], prepared of poly(vinyl alcohol) (PVA)/LDH nanocomposites under 2 h sonication of the related mixture of PVA and LDH with different concentrations. The prepared PVA/LDH nanocomposites showed better performance in the case of thermal and mechanical characteristics. While the obtained parameters from microscale combustion colorimeter including heat release capacity, total heat release, peak of heat release rate for the nanocomposite with 5% loading were $185\,J\,g^{-1}\,K$, $14.3\,kJ\,g^{-1}$, and $189\,W\,g^{-1}$, respectively. These data were $388\,J\,g^{-1}\,K$, $16.7\,kJ\,g^{-1}$, and $397\,W\,g^{-1}$ for the pure PVA and showed improved flammability of the nanocomposite. Meanwhile, based on the TGA, the temperature of 50% degradation ($T_{50\%}$) was increased from 290°C for the pure PVA to 347°C for the nanocomposite containing 1 wt% of LDH. On the other hand, mechanical features of the nanocomposites 1 and 3 wt% including tensile strength and elongation at break were all superior compared to the pure PVA. Therefore, strong and proper interactions between LDH and polymer lead to reinforcement of the resulted PVA/LDH nanocomposites.

In another study [66], the procedure of preparation of poly(methyl-ether-imide)/LDH nanocomposite has been reported as follows: the poly(amic acid) was first synthesized using 4,4′-{[(4-Tolylmethylene)bis(2,5-dimethyl-4,1-phenylene)]bis(oxy)}dianiline (TBNH) and 4,4′-oxydiphthalic anhydride (ODPA). Then, the various amounts of LDH were added to it. Herein, sonication was used for the fine dispersion. Finally, programmed heating was carried out for the imidization. Fig. 8, schematically demonstrate this route. Moreover, they claimed these nanocomposites have better resistance in the case of mechanical and thermal features.

Kalali et al. [67], functionalized LDH with several modifying agents including hydroxypropyl-sulfobutyl-beta-cyclodextrin (sCD), sodium dodecylbenzenesulfonate (DBS) as well as taurine (T) at the same time. They stated that to gain appropriate dispersion of modified LDH within the epoxy matrix a two-step route including a three-roll mill (30 min) and then sonication (20 min, 60°C) in acetone was used. After a thermally induced reaction among T and epoxy chains, the reaction mixture was cooled and then diaminodiphenylsulfone was added to it. At last, to attain nanocomposite thermal curing was performed. The nanocomposite containing unmodified LDH was also prepared based on a similar procedure for the comparison purposes. The behavior of the nanocomposites during a cone calorimeter test was studied. The obtained data from this test, e.g., time to ignition, fire growth rate index, and char residue confirmed better flame retardancy of the nanocomposite in the presence of the modified LDH. Higher char residue for the nanocomposite embedded with modified LDH creates a thick layer of char on its surface, which plays the role of an insulator and even prevents the surface to reach oxygen. In addition to that, the morphology of the remaining chars after cone calorimeter

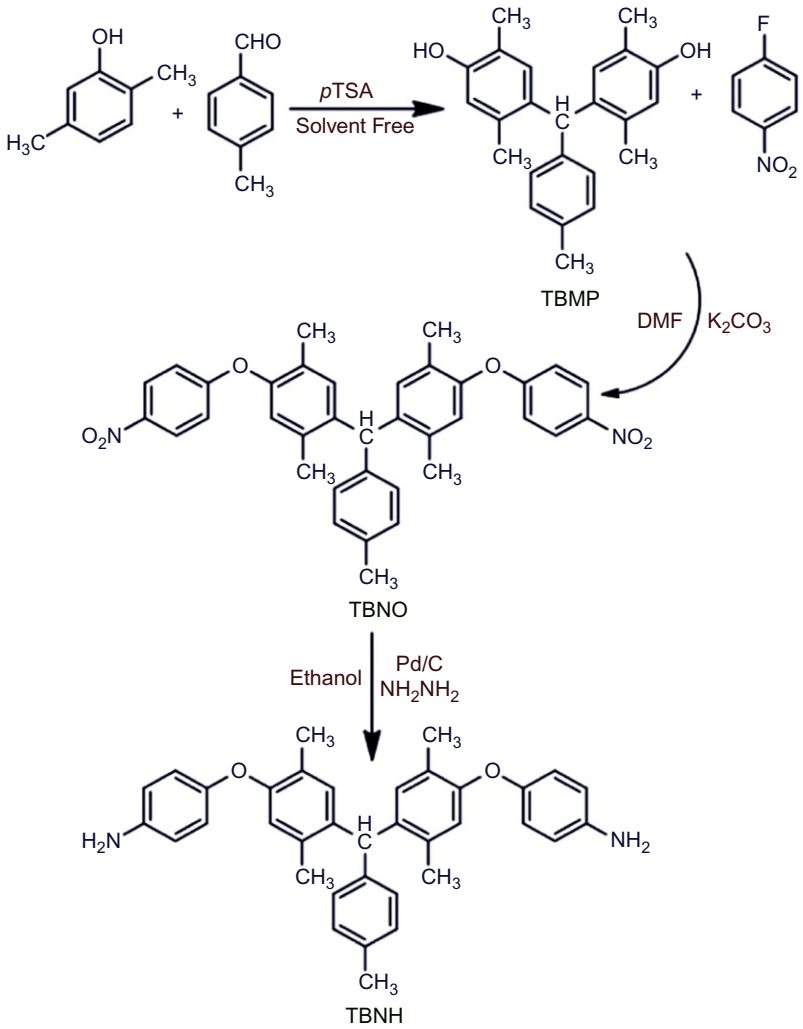

Fig. 8 Synthesis route of the diamine monomer. *Adopted from M. Shabanian, H. Ardeshir, S. Haji-Ali, H. Moghanian, M. Hajibeygi, K. Faghihi, H.A. Khonakdar, H. Salimi, Efficient poly(methyl-ether-imide)/LDH nanocomposite derived from a methyl rich bisphenol: from synthesis to properties, Appl. Clay Sci. 123 (2016) 285–291, with kind permission of Elsevier.*

test was investigated via scanning electron microscopy (SEM) and the resulted images showed that the char residue for the epoxy/LDH nanocomposite shows brittle nature, while nanocomposite containing sCD-DBS-T/LDH has a consolidated char layer prohibiting mass and heat transfer.

In another experiment, Mallakpour et al. [68] first intercalated LDH with vitamin B9 (VB9) under sonication. TEM images confirmed that the morphology has changed during surface modification. Then, it was mixed with an equal amount of Ag nanoparticles

via sonication for 60 min. The resulted Ag@VB9-LDH was used at 3, 6, and 9 wt% to be inserted within the CS matrix ultrasonically. The results of the antibacterial test showed their good performance against both Staphylococcus aureus and Escherichia coli.

Ultrasonication along with mechanical stirring was used to fabricate polystyrene (PS)/functionalized LDH nanocomposite [69]. At first stage, LDH was functionalized with MO and MB as the organic dyes. Next, a mixture containing both functionalized LDH and PS was subjected to the 2 h sonication and mechanical stirring. The TEM images revealed intercalation and in some cases, exfoliation for the LDH functionalized with MB. While in the case of the MO functionalized, some aggregations were detectable. The nanocomposite demonstrated high thermal resistance and smoke suppression characteristics.

Barkhordari et al. [70], designed carboxymethyl cellulose (CMC) capsulated Cephalexin (CPX)/LDH system with the aid of sonication. They first prepared LDH intercalated with CPX. Based on the XRD results and d_{003} spacing of 2.52 nm, it can be concluded that CPX molecules are arranged tilted with respect to the LDH. CMC/CPX/LDH Nanocomposite beads were prepared with the aid of sonication (bath) for 60 min. The prepared nanocomposite beads were applied for oral delivery of the CPX and results showed a controlled release of drug at conditions simulated to the intestinal tract. As can be seen from Fig. 9**,** compared to the CPX/LDH system liberating of the CPX occurred at a lower rate for the CMC capsulated CPX/LDH nanohybrids. The content of liberation was found to be 10%, 60%, and 22% at pH 1.2, 6.8, and 7.4, respectively.

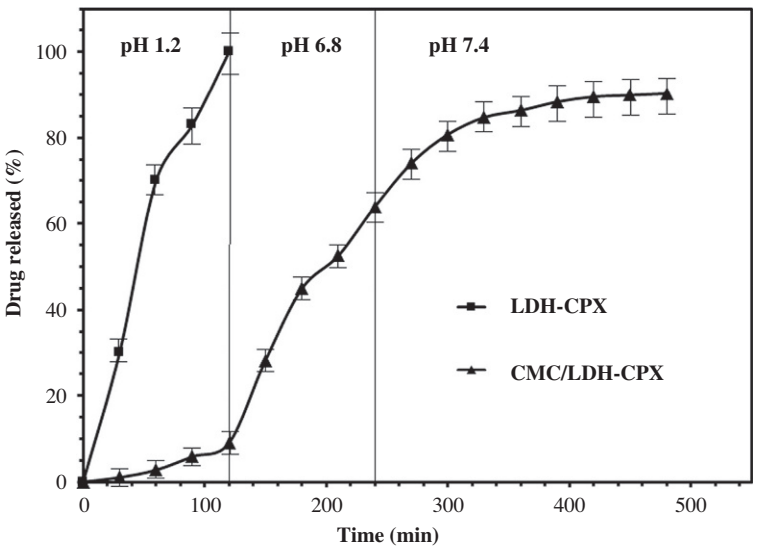

Fig. 9 Drug release behavior of LDH-CPX and CMC/LDH-CPX nanocomposite bead in conditions that simulate the gastrointestinal tract passage (pH and time). *CPX*, cephalexin; *CMC*, carboxymethyl cellulose. *Adopted from S. Barkhordari, M. Yadollahi, Carboxymethyl cellulose capsulated layered double hydroxides/drug nanohybrids for Cephalexin oral delivery, Appl. Clay Sci. 121 (2016) 77–85, with kind permission of Elsevier.*

In another study, Mallakpour et al. [71] prepared a series of nanocomposites with potential uses for the removal of Cd^{2+} from wastewater. An ultrasonic promoted coprecipitation strategy was first applied for the synthesis of multi-walled carbon nanotube (MWNT)/LDH nanohybrids. In the next stage, 1, 2, and 4 wt% of the prepared nanohybrid was added to the poly(ethylene terephthalate) (PET) solution and sonicated for 30 min to attain nanocomposites. From the TEM image of the PET/MWCNT/LDH nanocomposite 10 wt%, an exfoliated structure for the LDH can be imagined in the presence of the PET chains.

3.4 Other organics/LDH structures

Lyu et al. [72] applied ultrasonic bath in the process of functionalization of LDH with ionic liquid (IL). First, they let LDH interact with sodium dodecyl sulfate (SDS). After 4.5 h sonication of the obtained SDS/LDH in toluene, it was functionalized with trimethoxysilylpropanethiol. The resultant was subjected to a thiol-ene click reaction in the presence of 2,2-azobis(2-methylpropionamidine) dihydrochloride and 1-propylene-3-methylimidazolium chloride ionic liquid (IL) to prepare LDH functionalized with IL. The performance of the IL/LDH in the removal of Congo red (CR) was studied. As can be seen from curves of Fig. 10, the IL/LDH was more effective than SDS/LDH and the adsorption capacity was found to be 90.86 and 288.63 mg g^{-1} for

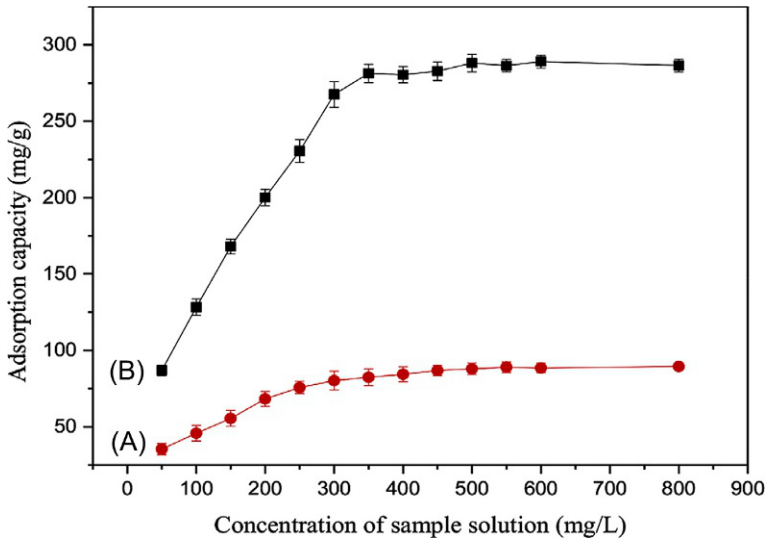

Fig. 10 Effect of the CR concentration on adsorption capacity (A) LDH-SDS; (B) IL-LDH (conditions: sample volume: 10 mL; pH of the sample solution: 7.0; amount of adsorbent: 5 mg; adsorption time: 60 min; temperature: 298 K). *CR*, Congo red; *SDS*, sodium dodecyl sulfate; *IL*, ionic liquid. *Adopted from H. Lyu, Y. Ling, J. Fan, Y. Chen, Y. Yu, Z. Xie, Preparation of ionic liquid-functionalized layered double hydroxide via thiol-ene click chemistry for highly efficient removal of azo dyes during broad pH range, J. Clean. Prod. 211 (2019) 1026–103, with kind permission of Elsevier*

the SDS/LDH and IL/LDH, respectively. The reason behind it is enhanced surface area and basal spacing as well as several interactions among the dye molecule and IL/LDH such as hydrogen bonding and electrostatic interactions.

Mallakpour et al. [73] fabricated LDH intercalated with organic diacids with the aid of ultrasonic irradiation as a green and fast technique. The prepared organo-modified LDHs are biocompatible with the capability to apply as proper nanofiller to prepare different kinds of environmentally benign nanocomposites. In another experiment [74], they intercalated LDH with VB9 using sonication for 1 h. The resulted organo-modified LDH was used as the nanofiller for the PVA matrix. For this aim, it was first mixed ultrasonically with TiO_2 and then 2, 4, and 8 wt% of the obtained was dispersed in water using sonication. After adding it to the PVA solution, it was irradiated further for 30 min to be prepared for casting. They claimed that the ultrasonic irradiation is an environmentally friendly approach for the preparation of the nanocomposites with potential use for the photodegradation of MB dye.

LDH was intercalated with a diacid fabricated from L-phenylalanine and pyromellitic dianhydride [75]. The resulted organo-modified LDH was inserted within the poly(vinyl chloride) (PVC) matrix to prepare nanocomposites with Cd^{2+} removal capability. Both processes of LDH modification, as well as its doping into the PVC matrix, were performed using ultrasonic irradiation as a green route.

In the study of Blaisi et al. [76], biomass-based composites were synthesized by insertion of date palm ash (DPA) with different concentrations within interlayers of LDH. To gain homogeneous and efficient dispersion of DPA into the interlayers of LDH, DPA was first ultrasonically dispersed (1 h) in deionized water and then was added to the solution containing related salts of the LDH. The DPA/LDH with a composition of 1.5 (g)/2 (g) showed a high removal percentage for the MO and eriochrome black-T. Based on the isotherm and kinetic investigations, chemical interactions among the carbonyl functional groups of the composites and dye molecules was occurred, which this finding was consistent with Fourier transform infrared spectroscopy.

It has been reported that ultrasonic can also be used to remove impurities in the process of surface modification. Hu et al. [77] reported washing the γ-aminopropyltriethoxysilane/LDH with ethanol in ultrasonic bath to omit the unreacted modifier. The obtained modified LDH was then used as the nanofiller to be incorporated in the polyaniline matrix to prepare anticorrosive coatings.

Marzec et al. [20], applied ultrasound to promote surface modification of LDH with different weight ratios of Alizarin as an organic dye. Two types of LDH were used with Mg/Al weight ratio of 30/70 and 70/30, which were labeled as LDH30 and LDH70, respectively. The resulted composites were inserted within the ethylene-norbornene (EN) and acrylonitrile butadiene-rubber (NBR) as the pigments. The resistance of the pigments against discoloration in several solvents was studied. As demonstrated in Fig. 11A, the pigment contained LDH30 with 10% of alizarin weight ratio, shows the best

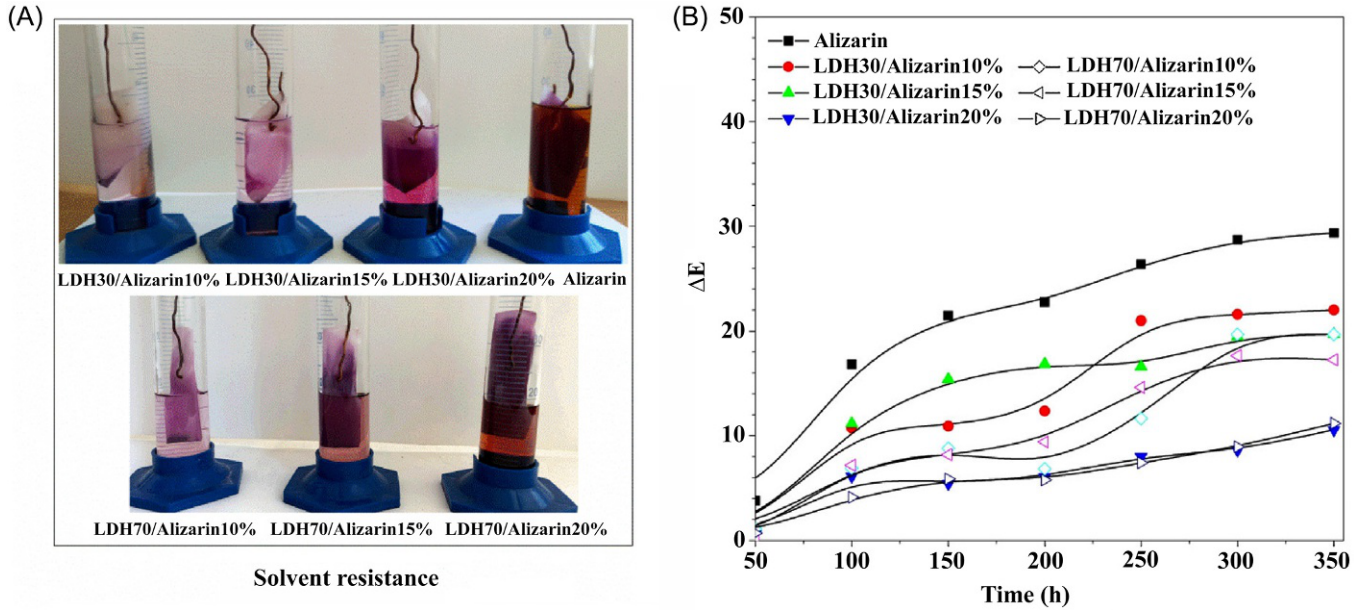

Fig. 11 Digital photographs of Alizarin, LDH30/Alizarin10% and LDH70/Alizarin10% after 24 h of immersion in acetone (A) and Color difference (DE) values for Alizarin and LDH/Alizarin pigments in ethylene-norbornene copolymer as a function of aging time (B). *Adopted from A. Marzec, B. Szadkowski, J. Rogowski, W. Maniukiewicz, M. Kozanecki, D. Moszyński, W. Maniukiewicz, M. Kozanecki, D. Moszynski, M. Zaborski, Characterization and properties of new color-tunable hybrid pigments based on layered double hydroxides (LDH) and 1, 2-dihydroxyanthraquinone dye, J. Ind. Eng. Chem. 70 (2019) 427–438, with kind permission of Elsevier.*

resistance since no significant color can be observed within the solvent after 24 h. In addition to that, color difference value, which is shown by △E for the Alizarin and Alizarin/LDH pigments in EN matrix vs aging time is presented in Fig. 11B. In the case of using Alizarin as the pigment, the amount of △E can be found to increase from 4 to 16 within 50 h confirming high photooxidation. While this parameter is considerably lower for composites embedded with the Alizarin/LDH pigments which demonstrate higher UV endurance for them. They acclaimed strong interactions among the LDH and dye molecule as well as dye insertion within the LDH intergalleries are responsible for these consequences.

4. Comparison of ultrasonication with other techniques

A comparative study of several techniques for the synthesis of organically modified LDH has been done. In a study done by Ezeh et al. [78], three different techniques, i.e., coprecipitation, sonochemical, and ultrasonic-assisted high-pressure hydrothermal were used for the preparation of the amine-functionalized LDH. After that, the effect of each technique on the physicochemical properties of the resultants was investigated. Results of CO_2 uptake measurements (Fig. 12) showed that first, the amine-functionalized LDH

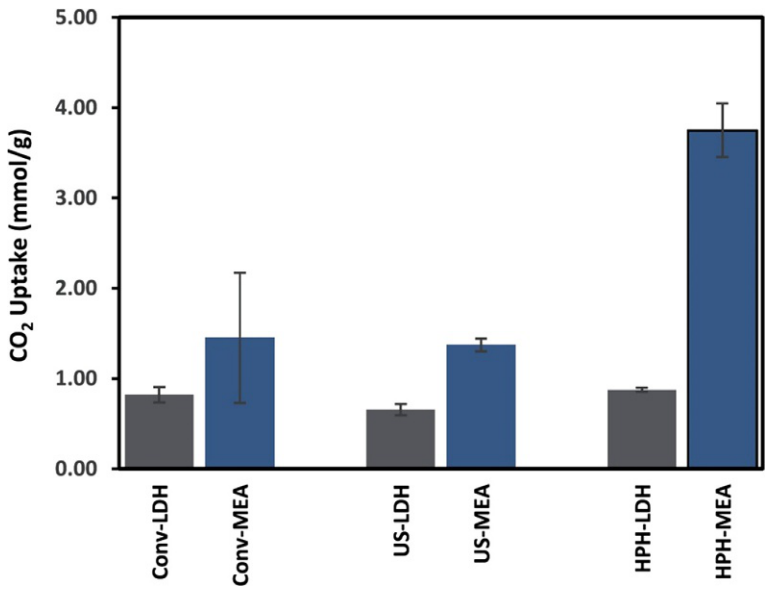

Fig. 12 Average CO_2 uptake of LDH and amine-modified LDH prepared via the different routes. *Adopted from C.I. Ezeh, M. Tomatis, X. Yang, J. He, C. Sun, Ultrasonic and hydrothermal mediated synthesis routes for functionalized Mg-Al LDH: comparison study on surface morphology, basic site strength, cyclic sorption efficiency and effectiveness, Ultrason. Sonochem. 40 (2018) 341–352, with kind permission of Elsevier.*

has better capacity compared to the unmodified one. Second, among three techniques used for the synthesis of amine-functionalized LDH, the ultrasonic-assisted high-pressure hydrothermal led to more efficient structures in the uptake process. This method not only enhances strong basic sites (O^{2-}) but also leads to a reduction in the number of moderate (M-O) and weak basic groups (OH^{-}). Totally, ultrasonic-assisted hydrothermal approach improves the textural properties of the adsorbent.

In the study of Quispe-Dominguez et al. [79] a comparison was performed among sonication-assisted masterbatch melt mixing and direct melt mixing efficiency on the dispersion of organically modified LDH within the poly(lactic acid). Several analyses were used to explore the effect of each technique. It was understood that sonication assisted route reflected better dispersion and a reduced amount of agglomerated LDH inside the polymer. They acclaimed the sonication-assisted masterbatch melt mixing method can be an efficient way for the synthesis of nanocomposites with high LDH amount benefits both solution mixing and melt mixing technique.

A study has been done by Nagendra et al. [80] on the effect of sonication on the dispersion of LDH in the polypropylene (PP) as well as characteristics of the resulted composites and it was compared with just stirring technique. They prepared two sets of composites, which differed in the step of pretreatment of the LDH before adding to the PP. In the first case, they prepared a gel from LDH by adding it to xylene and were stirred for 12 h at room temperature. In the second route, LDH was first dispersed in xylene using a sonication bath. The sonication time was 4 h and the temperature was maintained at room temperature. As demonstrated in Fig. 13A, the as-prepared LDH shows a hard contrast, which is representative of the presence of several layers. The mean size of the hexagonal platelets was 3.5 μm. The existence of water molecules within the layers of the LDH was confirmed by the domination of the oxygen peak in the energy dispersive spectrometer (EDS). In the TEM image of the prepared LDH gel in the first route, a delaminated structure is observable. The selected area electron diffraction (SAED) (inset of Fig. 13C) points out the single-crystalline nature of the delaminated nanosheets. Removal of the water molecules from the LDH interlayer can be concluded based on the reduction in oxygen peak in the EDS. The TEM image of the sonicated LDH is demonstrated in Fig. 13E. As can be seen, the platelets are broken to nanometer scaled sizes. In addition, the EDS spectrum of this sample shows a drastic decrease in the intensity of the oxygen peak, which confirms the removal of the interlayer water molecules. So, compared to conventional techniques like stirring, sonication not only leads to exfoliation of the LDH layers but also can reduce the size of the layers. As a result, the composite in which LDH was sonicated showed better thermal stability, nucleation ability, and higher crystallization rate of the PP compared to the non-sonicated system.

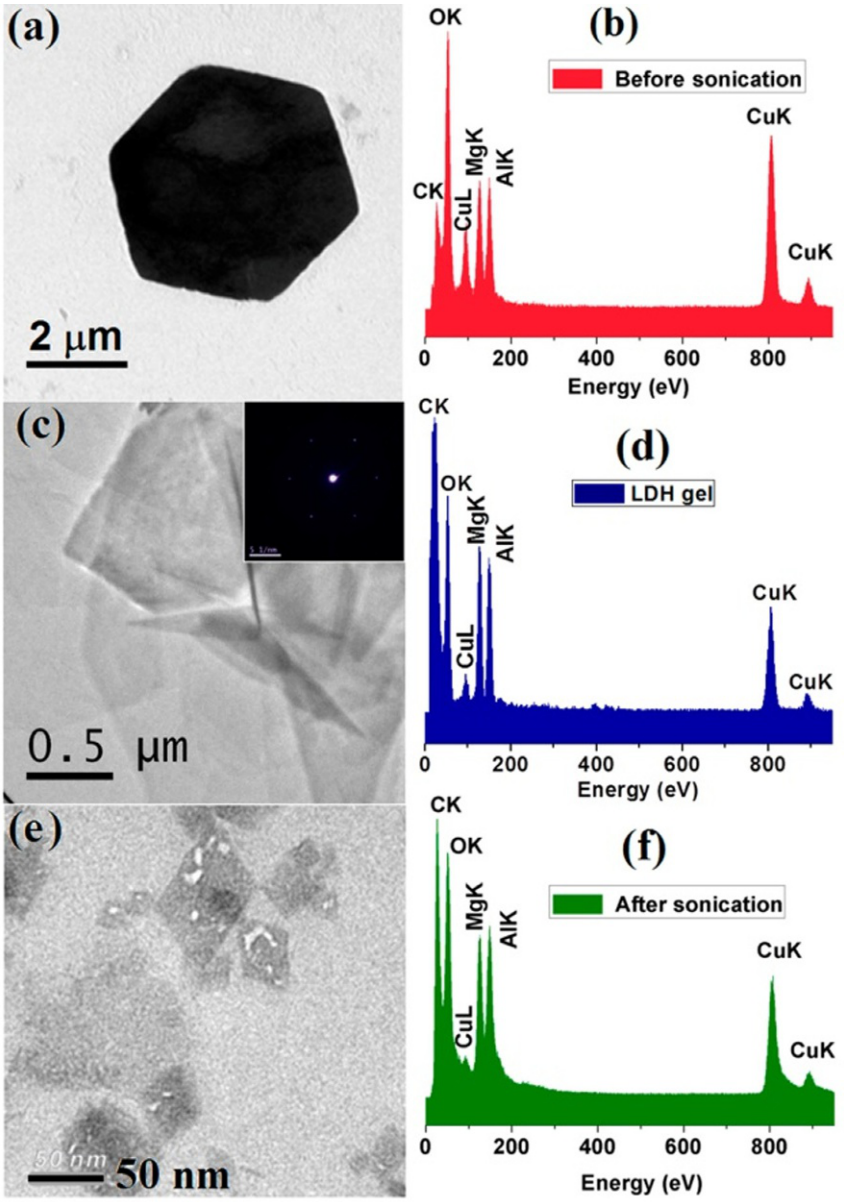

Fig. 13 TEM images of (A and B) as-prepared Mg-Al LDH and corresponding EDS spectrum, (C and D) delaminated Mg-Al LDH and corresponding EDS spectrum (inset) selected area electron diffraction (SAED) pattern of delaminated Mg-Al LDH, (E and F) sonicated LDH and corresponding EDS spectrum. *TEM*, transmission electron microscopy; *EDS*, energy dispersive spectrometer. *Adopted from B. Nagendra, K. Mohan, E.B. Gowd, Polypropylene/layered double hydroxide (LDH) nanocomposites: influence of LDH particle size on the crystallization behavior of polypropylene, ACS Appl. Mater. Interfaces, 7 (2015) 12399–12410, with kind permission of American Chemical Society*

With all these descriptions, in the case of synthesis of LDH composites based on the polymers, sonication can be a way to attain high-performance composites. Because rupture of polymer chains followed by the creation of free radicals caused branch points and creates high graft polymers via attaching lateral branches [81]. Several other studies have been paid to this subject and all are in agreement with this fact that sonication led to cross-linking and branching of the polymer matrix [82, 83]. This occurrence can modify several characteristics of the polymer composites such as some of the mechanical features [83].

5. Some disadvantages of sonochemistry

As we discussed in earlier sections, chemical reactions can be performed easier, faster, and in a better way by using ultrasound waves. In fact, sonochemistry is a powerful tool helps human to accomplish a reaction without using a surfactant and production of smaller particles without producing high temperatures. In fact, this method can convert harsh reaction conditions to a rather mild and gentle one [84]. But despite its versatile advantages, sonication can bring unwanted outcomes during its usage in chemical synthesis. Rodrigues et al. [85] pointed out the effect of sonication on the single-wall CNTs. In their study, a sonication device with 600 W power and 20-kHz frequency equipped with a horn was used to create a stable suspension of CNTs during filtration. They observed some damages on their walls. In some cases, these damages cut the (CNTs) and led to shortening their length. However, the outer wall was more exposed to the sonication damage and created an obstacle against damaging for the inner wall.

In some practical applications, sonochemistry faced with some difficulties. For example, in the conversion of chitin to CS, the ultrasonic route has been used instead of chemical techniques [86]. However, inhomogeneous directional ultrasound field limits its industrialization. Accordingly, to gain uniform distribution of the cavitational activity in large scale more than one transducer should be used [87].

6. Other applications of ultrasound

Apart from its usage for dispersion purposes in the procedure of surface modification of nanoparticles and the nanocomposites preparation, ultrasound has a variety of applications in other areas. For instance, Collins et al. [88] performed RAFT polymerization of acrylates and acrylamides using ultrasonic waves. Interestingly, they performed this in the absence of a conventional initiator like azobisisobutyronitrile. In their study, pyrolysis of the organic solvent which was done by the acoustic cavitation led to the formation of radicals having the role of the initiator. It has also a versatile application in medical sectors. For example, at low frequencies ultrasound can be used for gene delivery purposes [89]. Several studies have paid to some aspects of ultrasound-assisted disruption of the blood-brain barrier [90]. In the food industry, it has been widely used for several

purposes, e.g., crystallization of the milk fat [91], extraction of polyphenols from pomegranate peels [92], and inactivation of microbes of dried food ingredients [93]. In the extraction of bioactive materials from agro-wastes, it can be a good alternative route for the conventional Soxhlet extraction which has several limitations, e.g., consuming high amounts of the organic solvents, long time of extraction, and the probability of thermal degradation of the targeted material [94].

Sonochemistry helps human to treat industrial sludge and wastewater. In the sonolysis approach, microbubbles are formed as a result of acoustic cavitation. The sudden collapsing of these bubbles creates hot spots with high pressure and high temperature and as the result promotes destroying the toxic materials [95]. On the other side, it has been reported that it accelerates the degradation of dyes in the presence of a photocatalyst. In cases where the wastewater is nontransparent, it is difficult for the light to penetrate. Therefore, due to the low penetrating depth, the photocatalysis action faces trouble. Here, the role of sonocatalysis becomes important. The as-mentioned hot spots encourage the valence electrons of the photocatalyst to move from valence bond to the conducting bond and consequently enhance its catalytic proficiency [96].

7. Conclusions

Sonochemistry can be a proper replacement for traditional energy sources in a broad range of chemical reactions and synthesis. Taking into account the creation of hot spots, reactions can occur in a shorter time with higher yields with the aid of ultrasonic waves. On the other hand, it is one of the cheap and accessible facilities in all of the chemistry laboratories. Meanwhile, it is a green and safe tool without any environmental consequence. That's why it has been widely used in the synthesis protocols, surface modification of nanoparticles, and also for dispersion purposes in the preparation of nanocomposites. In this chapter, we specifically focus on the organo/LDH composites and some of the studies were done through the sonochemical approach in this area were presented. Meanwhile, different applications for the resulted composites were mentioned. Several results showed that it can be a key for the LDHs aggregation problem in the process of nanocomposites synthesis. Also, it can provide the energy required for the reaction among LDHs as well as the organic counterpart and promote reactions, which lead to several types of composites. However, during its usage, paying attention to several parameters related to sonication is crucial including time, power, frequency, and type of the transducer. All of these parameters have an effect on the resultant. Consequently, enough care and attention should be taken during its utilization. Eventually, more studies should be done to make sonochemistry more accessible even in industrial areas in the future.

Acknowledgments

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CHAPTER 11

Sonochemical protocol for the organo-synthesis of TiO_2 and its hybrids: Properties and applications

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1. Introduction

Nowadays, sonochemistry, as a simple route in the chemistry science, is commonly used for the numerous research domains such as organic synthesis, electrochemistry, environmental remediation, polymer chemistry, sonocatalysis, extraction, pharmaceuticals, food industry, construction of materials, and biomass conversion. Ultrasound is a sound field with a frequency higher than 20 kHz (Fig. 1) and is an effective method to homogenize, mix, and reduce the size of particles [1–6].

Fig. 1 Ultrasound range diagram. *Adopted from S. Arefi-Oskoui, A. Khataee, M. Safarpour, Y. Orooji, V. Vatanpour, A review on the applications of ultrasonic technology in membrane bioreactors, Ultrason. Sonochem. 58 (2019) 104633, with kind permission of Elsevier.*

Fig. 2 shows the utilization of ultrasonic power for the fabrication of materials for several years.

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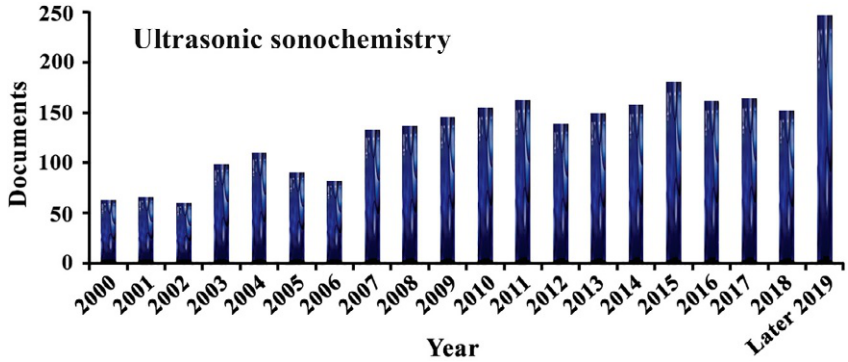

Fig. 2 Proportion of manuscript including "ultrasonic sonochemistry." *Data from Scopus website (May 2020).*

There is a link between sonochemistry and the rules of green chemistry, so, chemists around the world apply ultrasound to develop new applications based on it (Fig. 3) [7].

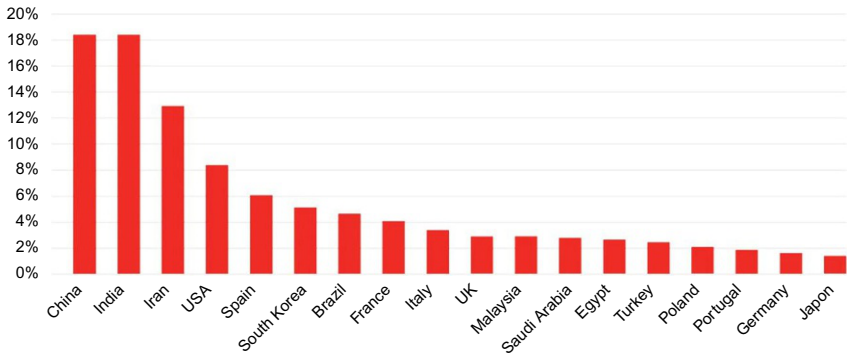

Fig. 3 Proportion of manuscript involving "ultrasound/sonochemistry" and "green/eco-friendly/sustainable chemistry" concepts in relation to the country where the study was conducted (from 2000). *Data from Scopus website (January 2017). Adopted from G. Chatel, How sonochemistry contributes to green chemistry?, Ultrason. Sonochem. 40 (2018) 117–122, with kind permission of Elsevier.*

This technology suggests several distinctive benefits compared to the conventional techniques. Greater selectivity, higher yields, enhanced reactivity, acceleration and decrease of reaction time, energy savings, cleaner products, and activation of catalysts are the benefits of ultrasound technology in comparison with other methods. Indeed, sonochemistry is a more efficient technology for the organic synthesis than photochemistry, hydrothermal, pyrolysis, and microwave-assisted chemistry [8–11].

In 1927, Wood and Loomis, for the first time, reported the effects of ultrasound on several phenomena, and so far, numerous applications of this technology for sustainable synthesis have been reported, for example, fabrication of amorphous materials such as metal oxides, the introduction of nanomaterials into mesoporous substances, and fabrication of nanomaterials for various usages [8–11]. Up to now, researchers used ultrasound for the construction of materials. For example, Okoli et al. [12] applied the sonochemical approach for the fabrication of metal-alloy nanoparticles (NPs) as electro-catalysts for electrochemical uses. Zahedi et al. [13] used ultrasonic irradiation for the preparation of chitosan NPs as polymeric nano-catalyst to synthesize dihydropyrroles. Naeimi et al. [14] prepared copper-based bio-composites for green oxidation of alcohols. Mallakpour et al. [15–18] used ultrasonic waves for the organo-synthesis, surface modification of NPs, and fabrication of various polymeric composites with antibacterial and remediation applications.

During the sonication process, three steps occur, which initially causes the bubble formation, then the bubble growth, and eventually, the bubble collapses as this step produces temperature up to 5000 K. Therefore, in order to better dispersing, de-agglomerating, homogenizing, blending, dissolving, as well as reducing the particle size of materials, ultrasound irradiation can be useful [19].

Ultrasound has diverse kinds of sonication: direct and indirect, which for direct sonication, horn system is used and for indirect sonication, bath (low intensity), as well as cup-horn systems (high intensity), are applied [20].

On the other side, titanium dioxide or titania (TiO_2), is a semiconducting metal oxide with white color and peculiar physic-chemical features like exceptional stability, biocompatibility, low cost, nontoxicity, easy preparation, and high activity. This material has various utilizations in photocatalysis, solar cells, sensors, electronic components, ceramics, catalysis, food, cosmetics, and are found in paints, ink, papers, and rubbers. Rutile, anatase, as well as brookite are three crystalline constructions of titania, which among them, anatase and rutile have prominent significance. Anatase and rutile have 3.2- and 3.0-eV band gaps, respectively [21–24].

Due to the excellent properties of TiO_2 as well as the useful ultrasonic usages, numerous TiO_2-based hybrids were prepared under sonication. In this chapter, we will especially focus on the role of ultrasonic irradiation for the organic synthesis of TiO_2 and their hybrids with diverse applications.

2. Effect of ultrasonic power in the organic synthesis of TiO_2 and their applications

Since TiO_2 has excellent photocatalytic property, it can be used for the photodegradation of pollutants like dyes. In this way, Miao et al. [25] synthesized mesoporous TiO_2 employing the skins of grapes, garlic, tomato, and onions as the bio-templates. Owing

to the high surface area of mesoporous TiO_2, it is an efficient material for dyes photodegradation. For the preparation of TiO_2, first, inorganic elements in the skins were removed with the help of acid chloride, after washing and drying the skins, they were added to a solution containing titanium tetraisopropoxide (TTIP). The ultrasonic bath was employed to exit the air bubbles and enter the solution containing TTIP into the skins. Afterward, the sample was added to water, and finally, it was filtered, dried, heated (to 450°C), cooled, and products were achieved. Advantage of this method was the use of sonochemical processing as a beneficial system and biological templates. The fabricated particles showed different morphologies and different photocatalytic behaviors.

Solano et al. [26] used lemongrass extract as a reducing agent, as well as a stabilizer for the preparation of TiO_2 NPs and also TiO_2 doped with Fe for utilization in the wastewater treatment. In the fabrication process, the TTIP precursor was added to the aqueous *lemongrass* extract under ultrasound processor. After calcination at 550°C, the product was gained. Based on the outcomes of ultraviolet-visible (UV–Vis) spectroscopy, the absorption edge of doped TiO_2 was greater than un-doped TiO_2. X-ray analysis confirmed the anatase phase of fabricated TiO_2, which was as a catalyst for photocatalytic processes in the wastewater remediation.

In another study by Yu et al. [27] mesoporous TiO_2 with anatase and brookite bicrystalline structures was prepared directly under ultrasound probe in the presence of a suitable copolymer, and the prepared mesoporous TiO_2 had a narrow pore size distribution. At first, TTIP and triblock copolymer were dissolved in alcohol. Then, it was stirred and added to deionized (DI) water under ultrasonic waves. After centrifugation, it was washed and dried. Ultrasonic waves were assisted in the preparation of the brookite structure. As an outcome of applying the polymer, the content of brookite phase increased, along with the crystalline and pore size of brookite and anatase. The prepared samples demonstrated superior photocatalytic activities compared to the commercial P25 for n-pentane degradation. The great activities of the samples were due to the good surface area, high content of brookite phase, and mesoporosity.

Wang et al. [28] reported the fabrication of mesostructured TiO_2 via ultrasound technique employing octadecylamine as a long-chain amine and TTIP precursor. Based on the microscopic investigations, particles with spherical morphology and low aggregations and size of 50–200 nm were achieved.

Also, Pinjari et al. [29] prepared and characterized nanostructured TiO_2 by employing both conventional and ultrasonic procedures for the examination of cavitational effects in the fabrication route. Also, the influence of calcination time (750°C for 30 min to 3 h) on features of fabricated particles was studied. With the difference in sonication time, interesting results were observed. With increasing ultrasonic time, initially, the content of rutile increased and then decreased after the optimization of sonication time. In general, using the ultrasonic process compared to conventional methods, TiO_2 particles with a

higher content of rutile were achieved. Thus, 3 h of calcination time and 10 min of sonication time were the best conditions to attain the 100% rutile TiO_2 with good morphological features.

3. Effect of ultrasonic power in the organo-modification of TiO_2 and their applications

One of the useful techniques to enhance the distribution stability of TiO_2 in different media and develop its properties is the surface treatment by various modifiers. Various materials can be used as modifiers, and some of them have been mentioned below, and examples are given for each group.

3.1 Silane coupling agents

Zhao et al. [30] applied two kinds of silane modifiers to improve the affinity and durability of TiO_2 to fabrics and investigated the effect of surface modification on TiO_2 features. For this aim, nano-TiO_2 was dispersed in DI water via ultrasonication (10 min) for preparation of the suspension. Diverse concentrations of silane coupling agents were added, refluxed, centrifuged, and washed for eliminating the extreme silanes. Then, the ultrasonic bath was used to re-disperse this centrifuged sample for better dispersion, and finally, the modified TiO_2 was dried. Thermogravimetric analysis (TGA) was used to estimate the efficacy of the modified particles in various reaction conditions. Fourier transform infrared (FT-IR) spectrometer outcomes confirmed the effective grafting of functional groups of the modifier to the TiO_2 surface by chemical connections. The modified TiO_2 showed increase in zeta potential due to the protonation of NH_2 groups in the acidic area. The reduction of polydispersity index and diameter of particles indicated that zeta potential affected on dispersion stability of particles.

In the study of Qi et al. [31], organosilane was used for grafting on the surface of TiO_2 via Si—O—Ti bonds. The modified particles were employed to produce cool materials based on a polymeric composite of TiO_2. During the process of hydrophobic modification of TiO_2, ultrasonic disperser and ultrasonic bath were applied. After modification, the water contact angle increased. Cooling feature and solar reflectance of the TiO_2 composites improved, significantly.

In another study, organo-silane was applied for surface functionalization of TiO_2 and improving the dispersion of filler in the cationic polymeric matrix. The ultrasonic bath was applied to disperse TiO_2 NPs in toluene, and after the addition of silane coupling agent, the mixture was refluxed, filtered, and washed. Indeed, by silanization reaction vinyl groups were attached on the particle surface for the creation of covalent bind between TiO_2 and polymer. By electron microscopy, the NPs were detected on the nanocomposite (NC) surface. The prepared NC was employed as a sorbent to remove arsenate from aquatic solutions. The NC containing a higher amount of TiO_2 revealed

greater sorption capability. Based on the kinetic and equilibrium experiments, this exothermic process was based on pseudo-second-order and Langmuir isotherm model [32].

Mallakpour et al. [33] used ultrasonic radiation and silane coupling agent to modify the nano-sized TiO_2 to enhance its distribution, as well as compatibility of inorganic and organic constructions. For this aim, a solution of silane coupling agent and TiO_2 suspension were blended and influenced via ultrasonication waves and finally, it was dried. During the modification, amine groups were introduced on the TiO_2 surface for connection to the organic matrix. Collected outcomes displayed that TiO_2 NPs homogeneously dispersed in an organic matrix.

Also, Dinari et al. [34] successfully functionalized TiO_2 NPs with three-dimensional silane modifier by employing ultrasonic irradiation. The functionalized particles were inserted into the polyamide matrix to prepare NCs as good adsorbents for Cr(VI) ion elimination from wastewater. The TGA outcomes proved the development in the thermal stability of NCs. Also, adsorption isotherms as well as adsorption kinetics were examined. Owing to the existence of diverse functional groups like nitrogen atoms, the fabricated NCs were good adsorbent for Cr(VI) ion removal.

In another study by Li et al. [35], ultrasound was used to prepare silane-modified TiO_2, and the modified NPs were incorporated into the fluoropolymer for the fabrication of NC coatings. The prepared samples were studied with many techniques and based on outcomes; the modified TiO_2 was dispersed in the polymeric matrix, homogeneously. Also, the modified particles developed corrosion resistance, self-cleaning features, as well as UV resistance of the NCs, effectively.

3.2 Dicarboxylic acid

Interaction between NPs and polymeric matrix can be improved by using dicarboxylic acid; actually, terminal carboxyl groups can change the van der Waals interaction to H-bonding with distribution facility and low energy attraction. In this regard, Gonzalez-Calderon et al. [36] used a pimelic acid modifier to enhance the interaction of nano-TiO_2 with isotactic polypropylene matrix. For coating the TiO_2 with pimelic acid, ultrasound waves were applied to prepare a homogenize mixture. Because of the chemical connections among the organic modifier molecule and nano-TiO_2 surface, the coating presented good thermal stability. The enhancement of the integration between the modified TiO_2 and polymer was seen in atomic force microscopy and dynamic mechanical analyzer.

Mallakpour et al. [37] modified nano-TiO_2 by amino acid-comprising diacids. For this aim, TiO_2 and bioactive diacids were mixed under agitation and methanol was used as a solvent. Then, this mixture was ultrasonicated, filtered, and washed. Under ultrasonic irradiation, aggregation decreased, and the dispersion of TiO_2 improved. The attained modified TiO_2 was characterized, and morphology studies displayed well-dispersed particles. This technique for modifying the TiO_2 was good for compatibility with a

hydrophilic surface. The obtained modified TiO_2 could be applied for manufacturing the various eco-friendly polymeric NCs.

Also, in another study, Mallakpour et al. [38] modified nano-TiO_2 with biologically active diacid via the ultrasonic process. Chemical connections among the diacid monomer and nano-sized TiO_2 was formed. The modified TiO_2, along with modified montmorillonite, were used as nano-filler for manufacturing the poly(vinylpyrrolidone) (PVP) NCs. Construction and features of the samples were studied, and field emission scanning electron microscopy (FE-SEM) studies indicated good dispersion of nano-filler in the PVP. The outcomes exhibited that the attained NCs had mainly intercalated construction, and they showed improved thermal stability in comparison to the neat polymer. Also, the existence of nano-TiO_2 along with nano-layer had a synergistic effect and improved the thermal behavior of the polymer.

3.3 Polymers

Currently, to avoid the aggregation of TiO_2 and enhance its dispersibility, the strategy of grafting or coating polymers on TiO_2 surface is often applied. Functional groups in the polymer chain can interact with OH on the surface of TiO_2 NPs and protect them from aggregation. Mallakpour et al. [39] used poly(vinyl alcohol) (PVA) for grafting on TiO_2 NPs to modify their surface for introducing into a polymeric matrix. To graft the polymer chain on the TiO_2 surface, nano-TiO_2 was dispersed in DI water using a magnetic stirrer and ultrasonic radiation. Then, a solution of PVA was prepared and added to TiO_2 suspension and irradiated under ultrasound power. Indeed, ultrasonic waves had outstanding dispersion effect on the functionalized TiO_2. Hydroxyl groups in the polymer chain reacted with OH groups of NPs and reduced the aggregation and enhanced the compatibility of NPs with the matrix.

Oliveira et al. [40] treated TiO_2 surface with PVA. Ultrasonicator was employed in modification process as a dispersant. Then, the modified TiO_2 was applied for the fabrication of nano-fluids. The obtained nano-fluids showed good thermal conductivity. Also, the resulted nano-fluids had greater viscosity compared to the water. Thus, modification of TiO_2 with PVA was a beneficial technique for stabilization of the obtained nano-fluids.

Polyaniline was used to modify the surface of TiO_2 by Li et al. [41] in order to develop the conducting behavior of this polymer in diverse areas. To this aim, aniline monomer with TiO_2 in the presence of HCl was sonicated to decrease the accumulation of TiO_2 NPs. After the addition of $FeSO_4$ and $(NH_4)_2S_2O_8$ as a strong oxidizing agent, the sample was stirred constantly. The polymerization was done, and finally, it was filtered and dried. The obtained products were characterized by many techniques and based on their outcomes strong connection happened at the interface of the polymer and TiO_2 NPs was concluded. Crystallinity and morphology of TiO_2 were fixed after modification and conductivity of the polymer improved.

Yousefzadeh et al. [42] used poly(hydroxyl ethyl aniline) for modification of nano-TiO_2 to prepare an adsorbent for elimination of Pb(II) ions from aquatic solutions. Chemical oxidization technique and ultrasonic treatment were used to synthesize the adsorbent. At first, TiO_2 was dissolved in HCl and ultrasonicated. After that, a solution of hydroxyethyl aniline was added and stirred in the presence of the oxidizing agent. Eventually, the sample was filtered and dried. The outcomes verified the crystalline structure of modified TiO_2 with 2.83 eV-band gap and 24-nm particle size. At pH 5.5, the adsorbent dosage of $2\,g\,L^{-1}$, and at 328 K, maximum adsorption happened. The best models for kinetic and thermodynamic were Webber-Morris and Langmuir. Also, Gibbs free energy had a negative amount, so the adsorption had an endothermic nature.

3.4 Other modifiers

Mallakpour et al. [43] covered the surface of nano-sized TiO_2 with serum albumin protein modifier as biocompatible protein to avoid agglomeration of the particles in the polymeric matrix (Fig. 4). For the modification process, ultrasonic irradiations were used for better distribution of NPs. The modified TiO_2 was introduced into poly(vinyl chloride) (PVC) matrix to prepare polymer-based composite in order to destroy methylene blue (MB) dye through photodegradation. The outcomes displayed a reduction of photocatalytic behavior of TiO_2 after modification and preparation of NCs. So, modified TiO_2 had UV shielding features and could protect the film from degradation.

Rahim-Abadi et al. [44] used ultrasonic irradiation to chemical modification of TiO_2 NPs with glycidyl methacrylate. For this aim, TiO_2, modifier, and $AlCl_3$ catalyst were mixed in tetrahydrofuran (THF) under ultrasonication. Then, it was stirred, centrifuged, washed with THF, and finally dried. A condensation reaction among epoxy functional group related to the modifier and –OH groups on the NPs was done, and the surface of TiO_2 was modified. TGA and FT-IR analyses proved successful modification. The modified TiO_2 was applied for the fabrication of NC films.

4. Sonochemical synthesis of polymeric hybrids based on TiO_2 and their applications

Sonochemistry can improve and develop chemical reactions through acoustic energy, which reduces reaction time and improves the speed of this process. Ultrasound, as a unique tool, opens up a manner for the manufacture of numerous polymer NCs in order to have two functions: both for filler dispersion in the polymeric matrix and polymerization of the monomer. Indeed, ultrasonic waves act as specific assistant and initiator to disperse the nanomaterials and to break the chemical bonds for increasing polymerization, respectively. Recent progress in the sonochemical construction of NCs with polymers and TiO_2 particles along with their physical features and different utilizations have been introduced [45].

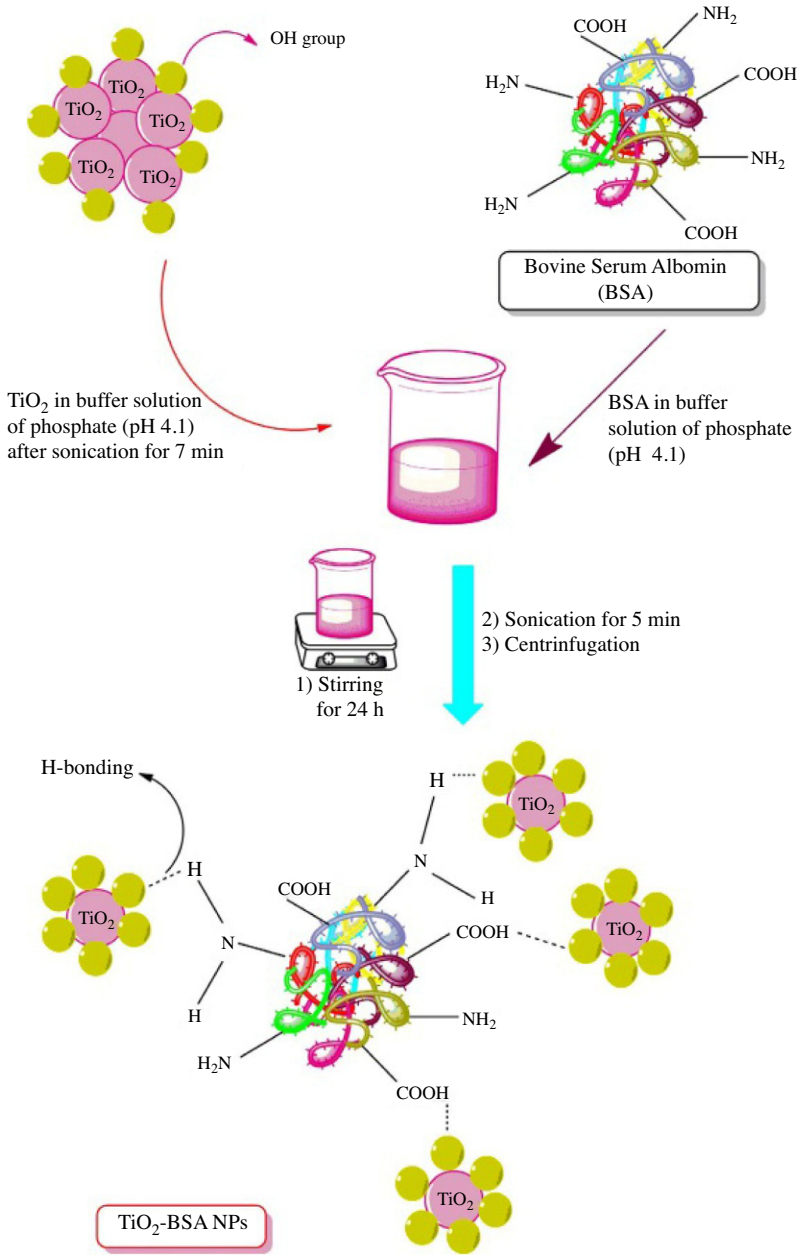

Fig. 4 Surface modification of TiO_2 NPs with BSA by ultrasonic irradiation. *BSA*, bovine serum albumin. *Adopted from S. Mallakpour, S. Shamsaddinimotlagh, Ultrasonic-promoted rapid preparation of PVC/TiO_2-BSA nanocomposites: characterization and photocatalytic degradation of methylene blue, Ultrason. Sonochem. 41 (2018) 361–374, with kind permission of Elsevier.*

4.1 Remediation industry

Water, as a valuable and vital material for human civilization, must be clean and free of toxic and harmful contaminants. Because of the toxicity of industrial dyes even at low concentrations, they must be removed from the water before they enter the body. On the other side, the presence of heavy metal ions such as cadmium, lead, chromium, arsenic in water is harmful and a major concern for human health. Several treatment techniques like precipitation, solvent extraction, filtration, photocatalysis, reverse osmosis, electrochemical, oxidation, adsorption, etc., have been applied for contaminants removal from wastewater. Adsorption is the most effective method for the wastewater treatment due to many advantages such as low cost, good selectivity, simple process, and elimination of pollutants even at low concentrations. Researchers around the world are constantly trying to develop efficient and cost-effective absorbents [46].

Based on published articles, a lot of research has been done to remove water pollutants with the aid of polymer/TiO_2 NC adsorbents, and ultrasonication technique has been used to make composites. For example, in many studies, TiO_2 NCs based on chitosan (CS) matrix has been fabricated due to the availability and low-costs of the CS and high surface area of the nano-TiO_2 to increase the adsorption capacity.

Bhanvase et al. [47] reported the synthesis of CS/ZnO/TiO_2 NC through sonochemical as well as conventional magnetic stirring. In the sonochemical route, the NC was prepared in three steps: fabrication of CS solution, preparation of ZnO/TiO_2 hybrid, and loading the CS on ZnO/TiO_2 NC, in which, ultrasonic irradiation was applied in all of the stages. For the preparation of the CS solution, ultrasonication was used with the time of 60 min. In the second stage (manufacturing of ZnO/TiO_2 NC) it was under ultrasound irradiation for 40 min. Also, for the construction of CS/ZnO/TiO_2 NC, the time required for the ultrasound-assisted route was 45 min. The fabricated NC was evaluated for the crystal violet dye adsorption from aqueous solution. The adsorption of dye for the fabricated NC through ultrasonic technique was significant in comparison to the conventional techniques. Indeed, ultrasonic waves dispersed the contents of NC uniformly to enhance the adsorption performance because of the physical influences of the ultrasonic waves for the fabrication of finely dispersed NC. The adsorption models were compared and based on them; the Temkin model was more suitable. Also, based on the kinetics investigation of adsorption phenomenon was fitted with the pseudo-second-order model. Furthermore, enthalpy ($\Delta H°$) and Gibbs free energy ($\Delta G°$) were positive and negative, respectively, which indicated endothermic and spontaneity adsorption phenomenon.

In another study by Vardikar et al. [48], ternary NC adsorbent based on CS, kaolin, and TiO_2 was prepared for dye adsorption. Both sonochemical and conventional methods were used in the manufacturing process of NC. The results showed that using an ultrasonic route, the average particle size of TiO_2 and NC were around 5 and 293 nm, respectively that were much less than conventionally prepared samples. Also, Brunauer-Emmett-Teller

(BET) analysis outcomes exhibited that the surface area of the ultrasonically prepared NC was 116.5 m^2/g, that was greater than the conventionally prepared NC (4.95 m^2/g). Moreover, 93.30% of dye was removed with ultrasonically prepared NC, and 85.50% was removed by conventionally prepared NC. So, ultrasonic had a good effect on the preparation and performance of the adsorbent. The adsorptive performance of NC matched with the Freundlich model and kinetic pseudo-second-order.

Alizadeh et al. [49] used ultrasonic irradiation for the fabrication of cross-linked magnetic adsorbent for the cadmium ion elimination and phenol degradation as harmful pollutants from the wastewater. For this aim, first, with the aid of ultrasonic vibration, magnetic NPs were dispersed in the CS solution. After mixing this solution with an emulsion containing DI water, emulsifiers, and hexane, a cross-linker [ethylenediaminetetraacetic acid (EDTA)] was added and magnetic EDTA-CS was obtained. Then under ultrasonication conditions using nano-TiO_2 in the presence of emulsifier the EDTA-CS-TiO_2 NC product was prepared. Based on the outcomes, the average size of the adsorbent was 40 nm, and according to the Langmuir model, the adsorption amount of cadmium was 209.205 $mg\,g^{-1,}$ and degradation yield of phenol was 90%. Also, after five cycles, adsorption capacities were in a good performance.

Zhou et al. [50] reported that composite hydrogel based on CS, nano-sized TiO_2, and poly(*N*-isopropylacrylamide) (TiO_2-CS-PNIPAAm), which could be applied as a promising and appropriate photocatalyst for acid fuchsin dye removal from solution. For the fabrication of composite hydrogel, NIPAAm, nano-sized TiO_2, and *N*,*N*′-methylenebisacrylamide cross-linking agent were added to the CS solution and mixed under sonication for 10 min to increase the distribution of the TiO_2 NPs. In the redox initiator system, initial polymerization was done, and subsequent polymerization (freezing polymerization) was completed at 18°C for 24 h. After the immersion of prepared hydrogel in water (for 24 h) for washing unreacted materials, it was freeze-dried, and the product was gained. Photocatalytic behavior of the composite hydrogel was tested for the dye degradation, and the outcomes specified that acid fuchsin adsorption dye was affected by pH. Protonation degree of the NH_2 groups in the TiO_2-CS-PNIPAAm is related to solution pH. Indeed, in the H^+ medium, the NH_2 groups that exist in the TiO_2-CS-PNIPAAm converts to ($–NH_3^+$), and electrostatic interaction exist between ($–SO_3^-$) acid fuchsin and $–NH_3^+$. In strong acidic solution (pH <4) $–SO_3^-$ converts to $–SO_3H$ and negative charges of acid fuchsin are decreased, and a weak interaction is created with composite hydrogel. As pH values increase (pH 4), negative charges ($–SO_3$) in dye structure rise and the interaction with composite hydrogel enhances and dye adsorption rate by composite increases. At pH 4, dye elimination rate was high (72.4%). However, in values higher than the optimum value (pH >4), the number of $–NH_3^+$ decreases and dye removal rate declines (Fig. 5). Also, the removal rate declined after raising the temperature. Based on kinetics studies, the adsorption of dye by the manufactured composite followed the pseudo-second-order model. Likewise, this composite hydrogel revealed great performance for the photocatalytic degradation of dyes.

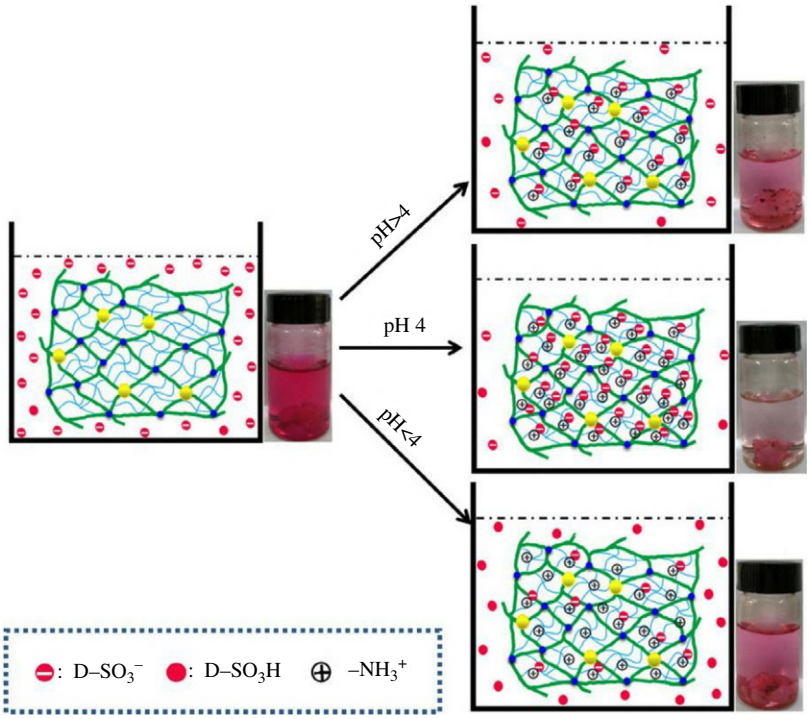

Fig. 5 Schematic illustration of AF dye adsorption from aqueous solution by nano-TiO_2/CS/PNIPAAm composite hydrogel under various pH conditions. *AF*, acid fuchsin; *CS*, chitosan; *PNIPAAm*, poly(*N*-isopropylacrylamide). *Adopted from J. Zhou, B. Hao, L. Wang, J. Ma, W. Cheng, Preparation and characterization of nano-TiO_2/chitosan/poly(N-isopropylacrylamide) composite hydrogel and its application for removal of ionic dyes, Sep. Purif. Technol. 176 (2017) 193–199, with kind permission of Elsevier.*

Seema et al. [51] demonstrated that bio-NCs based on cyclodextrin (CD), polycaprolactone (PCL), and TiO_2 (with weight percentages of 85%, 10%, and 5%, respectively) could be employed as adsorbents for Pb(II) elimination from wastewater. For the fabrication of bio-NCs, first, a biopolymer blend of CD and PCL was prepared using toluene as a solvent under continuous agitation. Nano-sized TiO_2, which was prepared with the sol-gel method, was added to the CD-PCL mixture and was stirred. The TiO_2 NPs were better dispersed and incorporated into the polymeric matrix by sonication. After drying the solution, the product was attained. BET results illustrated a high surface area for the NCs; thus, the adsorption capacity of the products was good. Transmission electron microscopy (TEM) micrographs displayed multi-morphological that comprise rod-like rectangular shapes. Additionally, the agglomeration of NCs was observed. According to the adsorption experiments, Pb(II) ion adsorption was affected by several factors like contact time, adsorbent dose, pH, and initial concentration of the solution. The optimum conditions were pH 9.7, 10 ppm pollutant concentration, and 0.005 g of the adsorbent. Adsorption isotherms and kinetic investigations were examined and based on the outcomes, adsorption was monolayer type (adsorption was obeyed by Langmuir isotherm). Also, Pb(II) ion was fitted with pseudo-second-order kinetics.

4.2 Packaging industry

In recent years, in order to protect foods, increase quality, prolonging the shelf-life, and prevent them from deterioration, active packaging-based biopolymer with antifungal and antibacterial features, has appealed increasing consideration compared to conventional packaging. Ethylene scavengers in active packaging preserve the quality and safety of products [52]. On the other hand, TiO_2 as an effective photocatalyst is an antimicrobial agent and suitable ethylene scavenger. Indeed, when TiO_2 exposed to UV light, it creates radicals like •OH, and $O_2^{-\bullet}$ that cause antibacterial properties. Thus, in the food industry, active packaging based on TiO_2 as harmless material and biopolymers have been synthesized. For example, Siripatrawan et al. [52] fabricated CS-TiO_2 NC film as active packaging. For this aim, a solution of CS was prepared by dissolving it in acetic acid. Nano-TiO_2 with several quantities was added, and then this solution was shaken and homogenized. Subsequently, using the ultrasonic processor, it was degassed. Finally, after casting on a ceramic plate, it was dried, and the film was gained. The scanning electron microscope (SEM) images indicated evenly distribution of nano-TiO_2 in the matrix. But, with the increasing NPs contents, spontaneous agglomeration was observed. Barrier and tensile strength features were enhanced, but optical transparency was reduced. The film ability for ethylene photodegradation was examined, and as demonstrated in Fig. 6, in the presence of light, the electrons promoted and went to the conduction layer and electron-hole pairs produced. After reaction with hydroxide ions or water, and radical species were formed and produced water and carbon dioxide from ethylene oxidation. The fabricated film containing 1% w/w TiO_2 revealed optimal ethylene photodegradation, barrier, and mechanical characteristics. Hence, it was selected for evaluation of antimicrobial, and antifungal behaviors and good results were achieved.

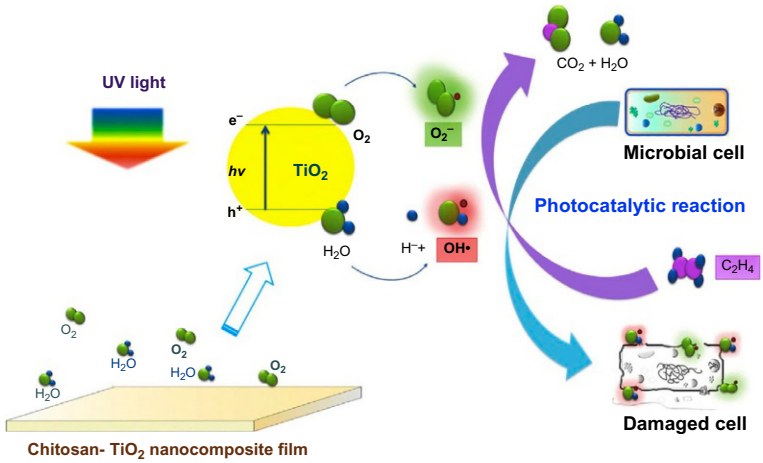

Fig. 6 A schematic diagram of the possible mechanism of photocatalytic degradation of ethylene and antimicrobial activity of the CS-TiO_2 NC film. *CS*, chitosan; *NC*, nanocomposite. *Adopted from U. Siripatrawan, P. Kaewklin, Fabrication and characterization of chitosan-titanium dioxide nanocomposite film as ethylene scavenging and antimicrobial active food packaging, Food Hydrocoll. 84 (2018) 125–134, with kind permission of Elsevier.*

Zhang's research team [53] introduced nano-sized TiO_2 in CS matrix and constructed the efficient antimicrobial composite film for foodborne microorganisms employing sonication. For this aim, CS and nano-TiO_2 powder were mixed together and dispersed in acetic acid through ultrasonic waves for 10 min. After that, for uniformity suspension, it was stirred and followed by adding epichlorohydrin as the cross-linker and was agitated for 4 h. After spreading the suspension on a plate and drying, it was peeled off from the plate and was immersed in NaOH solution. Lastly, was washed with DI water and dried. Morphological studies indicated the uniform distribution of TiO_2 into the matrix. The hydrophilicity and mechanical characteristics of the obtained CS-TiO_2 were enhanced, but, visible light transmittance decreased that assisted the photocatalytic antibacterial influence. Diverse pathogenic microbes (fungi, bacteria, and molds) were employed to estimate the antimicrobial action and based on the outcomes; the CS/TiO_2 composite had effective antimicrobial behavior against them. In order to investigate the utilization of the fabricated composite in the food packaging, red grape preservation was studied. They were effectively preserved by the prepared composite film and their shelf life was extended with this film (Fig. 7).

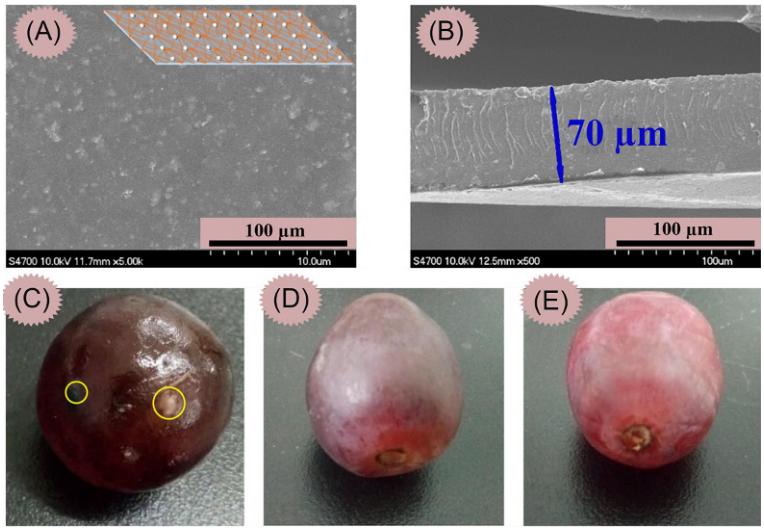

Fig. 7 (A) SEM surface image of CS-TiO_2 film with inserted schematic diagram, (B) SEM cross-section image of CS-TiO_2 film. Preservation of red grape packed in different materials at 37°C for 6 days, (C) plastic wrap, (D) pure CS film, and (E) CS-TiO_2 film. *SEM*, scanning electron microscopy. *Adopted from X. Zhang, G. Xiao, Y. Wang, Y. Zhao, H. Su, T. Tan, Preparation of chitosan-TiO_2 composite film with efficient antimicrobial activities under visible light for food packaging applications, Carbohydr. Polym. 169 (2017) 101–107, with kind permission of Elsevier.*

Sadeghi-Varkani et al. [54] used the ultrasonication and casting techniques for the preparation of novel bio-NC with embedding nano-TiO_2 particles into Lallemantia iberica mucilage (LM) as a cheap source of carbohydrate. LM biopolymer found in Asia and Europe was used as traditional medicine for the treatment of a variety of diseases such as hepatic, cough, fever, and renal sicknesses. To fabricate the composite, at first, via a magnetic stirrer, TiO_2 NPs were distributed and mixed in distilled water. After that, to impede the NPs aggregation, ultrasonic homogenizer was employed for 5 min. In the next step, the TiO_2 solution was added to the biopolymer solution and stirred for homogenizing and uniform distribution of particles. In order to eliminate the trapped air bubbles in the sample and for separation of any aggressions of NPs, ultrasonic treatment was used. After pouring and dehydration of the prepared solution, the film was formed. Thickness, mechanical, barrier, thermal, and optical features of the constructed NCs, which are the key parameters in the packaging industry, were thoroughly examined. Morphological studies indicated the good distribution of TiO_2, which led to the improvement of the gas permeability. Moisture absorption isotherms under different humidity's conditions showed stable behavior in NCs. Mechanical tests specified the improved features due to strong interaction among particles and polymer. But under high concentration of TiO_2, accumulation happened, and the useful mechanical, as well as structural characteristics, were diminished.

Teymourpour et al. [55] used the ultrasonic bath to disperse and homogenize TiO_2 NPs in DI water for construction of NC film using soybean polysaccharide matrix. Mechanical, barrier, thermal, and antibacterial features of the fabricated NC films were investigated. After the incorporation of TiO_2 into the matrix, barrier properties for water vapor, oxygen, and moisture decreased, mechanical features of the films enhanced, also, bio-NC films showed exceptional antimicrobial behavior against bacteria.

In the study of Baek et al. [56] poly(lactic acid) (PLA) was used as a matrix to prepare the TiO_2/polymer NC employing the sonochemical technique. To fabricate the PLA/TiO_2 film, at first TiO_2 surface was functionalized with oleic acid to make it nonpolar and increase the compatibility of them with PLA. Then, the modified TiO_2 was dispersed in chloroform, and it was mixed with PLA solutions. After that, it was sonicated and thoroughly agitated. Finally, on a glass plate, the prepared solution was cast and dried. Morphological pictures did not show aggregation. Based on the barrier feature, O_2, and H_2O vapor permeability reduced relative to the pure polymer. The flexibility and transparency of the fabricated film containing modified TiO_2 were higher than the PLA/TiO_2. Thus, TiO_2 functionalization developed TiO_2 dispersion in the matrix. This fabricated film had the potential to be used in food packaging domain.

Goudarzi research team [57] applied ultrasonic homogenizer for TiO_2 dispersion in water to prepare the TiO_2 suspension. After that, this suspension was mixed with a starch solution to develop the photodegradable and photo-producible bio-NC for food packaging. As a result, the absorption and content of moisture decreased with the help

of TiO_2 and UV ray. Also, photodegradability of this NC was exceptionally improved by simultaneous usage of TiO_2 and UV.

Bio-NC film with antibacterial and antioxidant features was prepared using incorporation of TiO_2 NPs and rosemary into the polymeric matrix of whey protein/cellulose nanofibers by Alizadeh-Sani et al. In the fabrication process, ultrasonic probe sonicator was used for the better distribution and complete homogenization of TiO_2 in the matrix. The antioxidant, antibacterial, and physicomechanical features of the NC film were studied, and the influences of several concentrations of cellulose nanofibers, TiO_2, and rosemary oil were considered in the film. The optimum quantities of TiO_2, rosemary oil, and nanofibers were 1%, 2%, 7.5%, respectively, to develop the functional features of the whey protein films. The outcomes revealed outstanding effects of a simultaneous mixture of TiO_2 and rosemary oil with matrix on the considered characteristics. Water resistance and mechanical feature of the films enhanced considerably after adding rosemary oil and TiO_2. Furthermore, the resulted bio-NC films demonstrated a noteworthy antioxidant as well as antibacterial behavior, and among bacteria, Gram-positive bacteria were more affected. Indeed, the manufactured films revealed good morphology and physicomechanical features. Also, owing to the outstanding distribution of rosemary oil and TiO_2 in the matrix, antibacterial, and antioxidant features, that are the key features in packaging usages, were gained [58].

Goudarzi et al. [59] in another work reported successful construction of starch-kefiran-TiO_2 bio-NC film as food packaging material via photochemical reactions. In the first step, equal ratios of kefiran and starch solutions were mixed under agitation for 15 min in the presence of glycerol plasticizer. Then, TiO_2 particles were dispersed in water under stirring (for 15 min) and sonication process was carried out through ultrasonic homogenizer (for 30 min) for the good suspension formation. TiO_2 suspension and film-forming solution agitated under UV-A exposure. After casting and drying, the NC film was attained. UV irradiation as a modification method, which is easy and green, enhanced the compatibility of kefiran and starch. By increasing photo-irradiation, the tensile strength of NCs improved. Young's modulus, elongation at break, and moisture-sensitive parameters reduced.

4.3 Other NCs and their applications

Xiang and Zhang [60] introduced several loading amounts (0, 1, 2, and 3 wt%) of TiO_2 NPs into acrylonitrile/styrene/acrylate (ASA) terpolymer through in situ polymerization method. In the NCs fabrication process, ultrasonic disperser was applied to disperse and reduce the accumulation of TiO_2 and then, the polymerization was done after adding the initiator to the reaction mixture. Based on TEM micrographs, after loading 1 wt% of TiO_2 in ASA, uniform dispersion was observed, but with the increasing TiO_2 amount, dispersibility declined due to the agglomeration of NPs. The influence of inserted TiO_2

NPs on the mechanical characteristics such as tensile features as well as impact toughness of the fabricated TiO_2/ASA NCs was examined. Based on the outcomes, when TiO_2 content was 1 wt%, a significant enhancement in the impact strength, and tensile strength was gained. This outstanding development was due to the better dispersibility of TiO_2 that mostly was related to the effect of ultrasound disperser before the polymerization of the monomer. Also, in situ polymerization causes better dispersion of TiO_2 in ASA.

In many studies, the ultrasonication method was applied for both the surface treatment of TiO_2 and fabrication of various TiO_2/polymer NCs. For instance, in studies by Mallakpour and Shamsaddinimotlagh, the surface of TiO_2 NPs was modified with bovine serum albumin (BSA) as a green coupling agent through sonication process. For this aim, at first, a buffer solution was prepared; nano-TiO_2 was added to it and then was sonicated for 7 min. Then, it was mixed with a buffer solution containing BSA using ultrasonication for 5 min. So, at this stage, BSA covered the surface of TiO_2 by ultrasonic waves. After centrifuging, washing, and drying, the modified powder was gained, in which 3, 6, and 9 wt% of this product was incorporated into the PVC using ultrasonication (for 7 min) for manufacturing the PVC/TiO_2-BSA NCs. Therefore, sonication manner was vital and very useful. Morphology examinations displayed the proper distribution of particles in the matrix. Also, based on outcomes, the fabricated NCs were more thermally stable than the pristine PVC. The photocatalytic test was done via MB degradation, and the outcomes indicated a decrease in the photocatalytic activity of the TiO_2 NPs after modification and insertion in the matrix due to the increase in the NPs size [43].

In another study, ultrasonic irradiation was employed to modify the surface of TiO_2 NPs with g-aminopropyltriethoxy silane (KH550) coupling agent and produce the polymer NCs-based PVA matrix. For this purpose, in brief, TiO_2 particles were first sonicated with KH550 solution for surface treatment of TiO_2. Then, 5, 10, 15, and 20 wt% of modified-TiO_2 particles were mixed with 0.1 g of PVA in the absolute ethanol as the solvent and was sonicated for 2 h. The fabricated NCs were used as electrolyte additive for the methanol oxidation reaction. The outcomes exposed enhancement in electrocatalytic behavior of Pt for the oxidation of methanol [61]

Ultrasonication process was used to modify TiO_2 surface with vitamin B1 as a natural molecule by Mallakpour and Adnany Sadaty (Fig. 8) [62]. For this purpose, nano-TiO_2 and VB1 in DI water were dispersed and homogenized, separately using ultrasonic irradiation (for about 15 min). Then, they were mixed together using the ultrasonic process to graft the VB1 modifying agent onto the nano-TiO_2 surface through several interactions between OH and NH_2 functional groups and OH groups on the TiO_2 surface. Actually, ultrasonic waves generated extra energy and caused a better interaction among modifier and TiO_2 in order to prevent accumulation. Then, PVC NCs were manufactured by inserting TiO_2 NPs using ultrasonication. Microscopic studies showed a uniform distribution of NPs into the PVC. Thermal and mechanical analyses exhibited enhancement in the characteristics of the NCs.

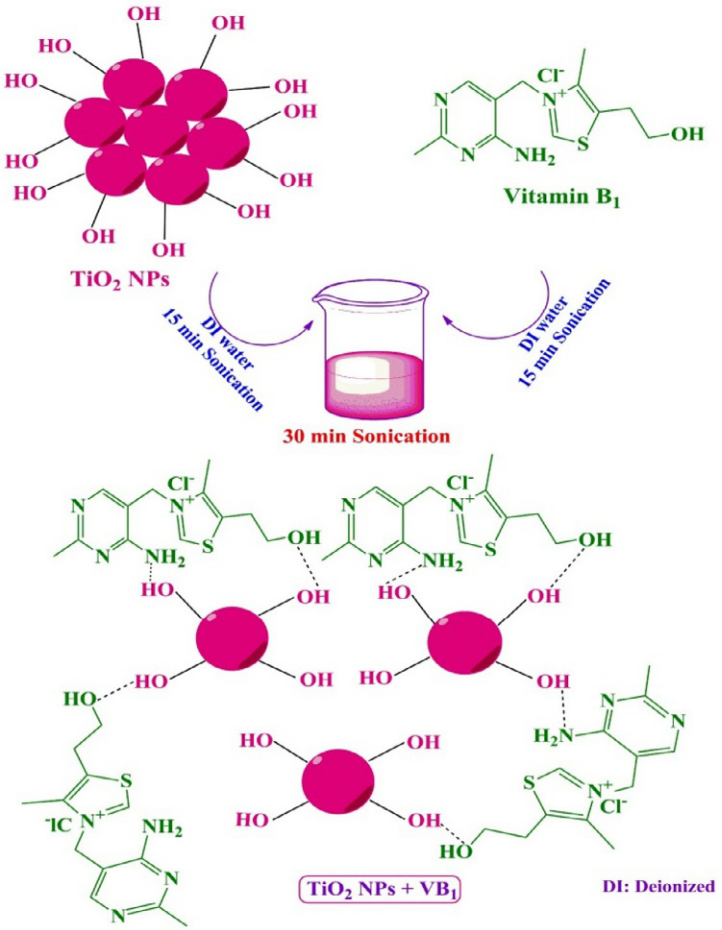

Fig. 8 Surface modification of TiO_2 NPs with VB1. *VB1*, vitamin B1. *Adopted from S. Mallakpour, M.A. Sadaty, Thiamine hydrochloride (Vitamin B1) as modifier agent for TiO_2 nanoparticles and the optical, mechanical, and thermal properties of poly(vinyl chloride) composite films, RSC Adv. 6 (2016) 92596–92604, with kind permission of The Royal Society of Chemistry.*

Also, in another study by Mallakpour and Khani [63], the ultrasonic tool was used for organo-modification of TiO_2 with biodegradable chiral diacid coupling agent and incorporation of organo-modified TiO_2 into the thermosetting poly(amide-ester-imide) matrix. Nano-sized TiO_2 was ultrasonicated with modifier solution for 30 min to better dispersion and interactions between TiO_2 and diacid functional groups. For the construction of related NCs, the organo-modified TiO_2 was added to the polymer suspension under sonication (4 h) for improvement of the distribution of particles in the polymer solution.

Mallakpour and Madani [64] reported the use of ultrasonic technique for the organo-modification and synthesis of CS/nano-TiO_2 NCs. Nano-TiO_2 was modified under ultrasonic waves by an amino acid modifier, and after that, in order to prepare the

NCs, CS powder was dissolved in acetic acid under sonication process for 30 min. Different amounts of nano-TiO_2 particles were sonicated in water to produce a suspension of TiO_2 for 1 h. After that, these prepared suspensions and CS solution were stirred and ultrasonicated for 1 h to obtain a homogenous mixture. Finally after drying, the NCs were gained. It was observed that the organo-modified TiO_2 distributed uniformly into the CS. Also, mechanical as well as thermal features of the NCs were more than the pristine CS. These NCs might be used to remove environmental pollutants.

Gonzalez-Benito et al. [65] used the sonication process for the preparation of thermoplastic NC with bactericide features and fiber-like structure based on poly(vinylidene fluoride) (PVDF) and several contents of TiO_2 NPs (0%, 1%, 2%, 5%, and 10%) to improve aggregation of NPs in the polymer solution. Solution blow spinning as a new procedure for spinning nano-fibers was employed to manufacture the NCs. The results exhibited good dispersion of NPs in the PVDF matrix.

Safaei and Taran [66] constructed bio-NC based on sodium hyaluronate (SH) biopolymer and TiO_2 NPs in the presence of ultrasound and then, examined the antifungal features of the product. SH was prepared through bacterial fermentation, and TiO_2 particles were synthesized by a sol-gel procedure. In situ technique was employed to synthesize the SH/TiO_2 NC. At first, SH and TiO_2 particles were sonicated separately in order to attain efficient homogeneity and good dispersion. After that, the solution containing TiO_2 particles was added dropwise to SH solution under agitation. The outcomes showed well distribution of NPs in the SH biopolymer and also, antifungal behavior of the bio-NC was better than the constituents. The constructed product had good antifungal behavior due to the synergistic influence of polymer and TiO_2 particles. TEM micrographs showed the formation of SH-TiO_2 NCs (Fig. 9).

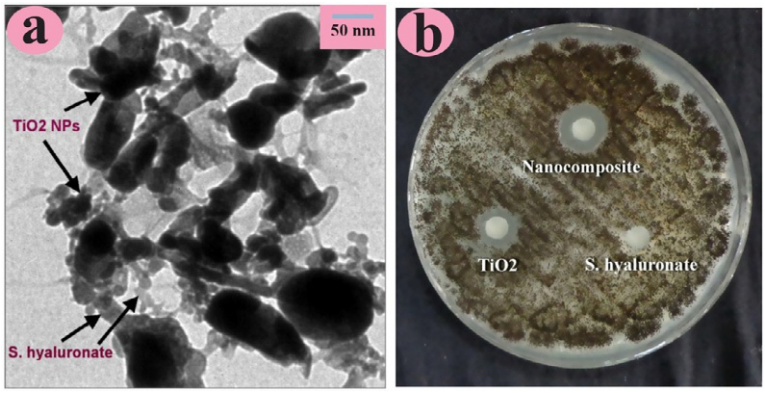

Fig. 9 TEM images of sodium hyaluronate-TiO_2 nanocomposite (A), antifungal activity of the sodium hyaluronate, TiO_2 NPs and sodium hyaluronate-TiO_2 NC against *Aspergillus niger* (B). *TEM*, transmission electron microscopy. *Adopted from M. Safaei, M. Taran, Fabrication, characterization, and antifungal activity of sodium hyaluronate-TiO_2 bionanocomposite against Aspergillus niger, Mater. Lett. 207 (2017) 113–116, with kind permission of Elsevier.*

One of the features of TiO_2 is self-cleaning behavior, which can be used for the preparation of self-cleaning fabric. So, Ghobashy [67] used ultrasonic and gamma waves as a good dispersant tool for TiO_2 distribution on the poly(ethylene terephthalate) (PET) fabric. Also, due to the low adhesion of TiO_2 on the fabric, poly(acrylic acid) (PAAc) as hydrophilic polymer was grafted onto the PET for better adhesion and generate oxidized species for pollutant removal. Finally, TiO_2@PET-g-PAAc fabrics were successfully achieved (Fig. 10). X-ray studies indicated rutile and anatase TiO_2 and morphological pictures showed good adherent and uniform distribution of TiO_2 and PAAc with fabric. Also, the thermal property of the constructed hybrid was increased. Three classes of dyes were selected as models for evaluation of the self-cleaning, and the good results were gained.

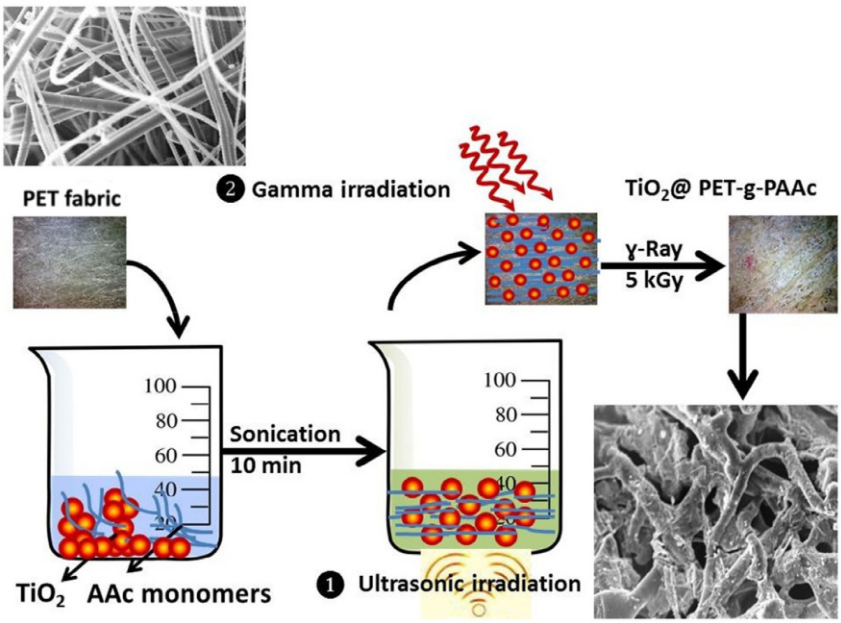

Fig. 10 Demonstration of PET fabric modification set up. 1-Ultrasonic irradiation, 2-Gamma irradiation. *PET*, poly(ethyleneterephthalate); *PAAc*, polyacrylic acid. *Adopted from M.M. Ghobashy, Combined ultrasonic and gamma-irradiation to prepare TiO_2@PET-g-PAAc fabric composite for self-cleaning application, Ultrason. Sonochem. 37 (2017) 529–535, with kind permission of Elsevier.*

TiO_2-biochar NC, as proficient sono-catalyst for Reactive Blue 69 degradation, was prepared by Khataee et al. [68]. The prepared NC presented excellent surface area as well as pore volume for high sono-catalytic performance. At pH 7, 300 W of ultrasonic power, and 1.5 g/L loading of NC, the best efficiency (97.5%) was gained. Utilization of titanium above neutral pH, its stability in NC, and small dissolved concentration of it are the remarkable advantages of the fabricated NC.

In the research of Saber-Samandari et al. [69], 3D NC scaffolds were prepared, which were including TiO_2 NPs (in different amounts), cellulose, and hydroxyapatite, as a replacement for bone-tissue engineering. The sonication power was applied to fabricate the scaffold. Mechanical, swelling behavior, and cytotoxicity of the NC were examined and based on outcomes, it had highly porous construction, and in high TiO_2 amount, the mechanical property was suitable. After increasing the TiO_2 percentage, swelling behavior was lesser. From cytotoxicity tests on L929 cells in SEM image, this fabricated scaffold was biocompatible and nontoxic (Fig. 11).

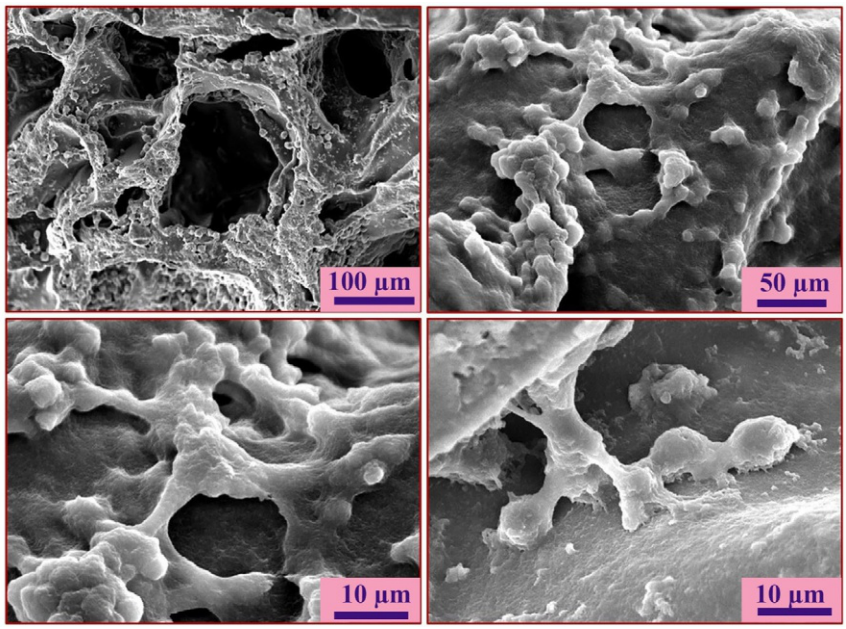

Fig. 11 SEM of L929 cells seeded on the surface of NC samples. *Adopted from S. Saber-Samandari, H. Yekta, S. Ahmadi, K. Alamara, The role of titanium dioxide on the morphology, microstructure, and bioactivity of grafted cellulose/hydroxyapatite nanocomposites for a potential application in bone repair, Int. J. Biol. Macromol. 106 (2018) 481–488, with kind permission of Elsevier.*

Yu et al. [70] prepared polyaniline/TiO_2 composite under ultrasound processing and deposited it on the cotton fabric surface. This fabricated sample had UV protection, photocatalytic behaviors, as well as sunlight absorption. The conductivity of the fabricated composite was investigated, and the outcomes displayed respectable conductivity, which was reduced somewhat after increasing the TiO_2 percentage.

Noman et al. [71] used the ultrasonic acoustic technique for deposition of TiO_2 NPs on the cotton surface. The features of manufactured samples like self-cleaning, antimicrobial, mechanical, and washing durability were examined. The outcomes revealed the

insertion of anatase TiO_2 (with 4-nm particle size) and admirable photocatalytic behavior. After 30 times home launderings, self-cleaning efficiency of the fabricated fabric showed exceptional washing durability. Ultrasonic waves had no undesirable influence on the mechanical feature of NC. Washing durability revealed the acoustic cavitation role as well as covalent connections among –OH on the cotton and TiO_2 particles.

Due to the harmfulness of traditional inks, attention has been given to edible inks. For example, Wang research team [72] prepared edible ink of CS/TiO_2 NC for utilization in the printing field. In the preparation process, ultrasonic treatment (1 h) was employed to disperse edible pigment TiO_2 in water, and then it was added to a solution of CS under agitation. To prepare sustainable and stable ink, methylcellulose and Tween 80 as low-cost, easy access, and green stabilizers were used. Fitting, print quality, and rheological features of the prepared ink were studied. Fastness, optical density, and scratch-resistance of the ink were satisfactory. This ink was proper to screen-print and customization options, and also drug or food decoration. Fig. 12 shows screen-printed ink on the black cardboard.

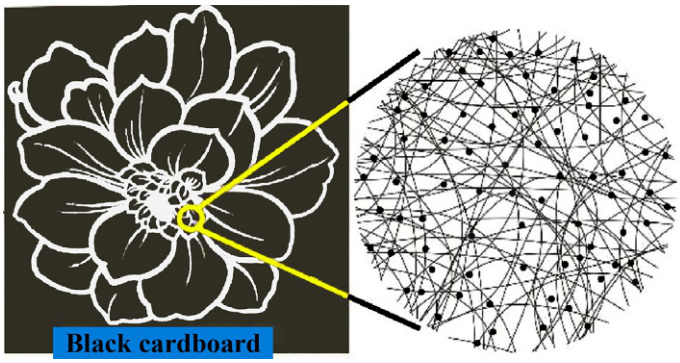

Fig. 12 Application of CS/TiO_2 composite ink. *Adopted from H. Wang, J. Qian, H. Li, F. Ding, Rheological characterization and simulation of chitosan-TiO_2 edible ink for screen-printing, Prog. Org. Coat. 120 (2018) 19–27, with kind permission of Elsevier.*

An et al. [73] used nano-fibrillated cellulose (NFC), Fe_3O_4, as well as TiO_2 NPs for the successful construction of NC for the photocatalytic generation of hydrogen. All stages of production of this composite and its utilization are observed in Fig. 13. To prepare the composite, ultrasonic treatment was employed for uniform dispersion of NFC in aqueous solution. Morphological investigations revealed uniformly loading of NPs on the NFC support. According to outcomes, by using NFC as versatile support and useful titania NPs, photocatalytic efficiency, as well as the recyclability, were enhanced.

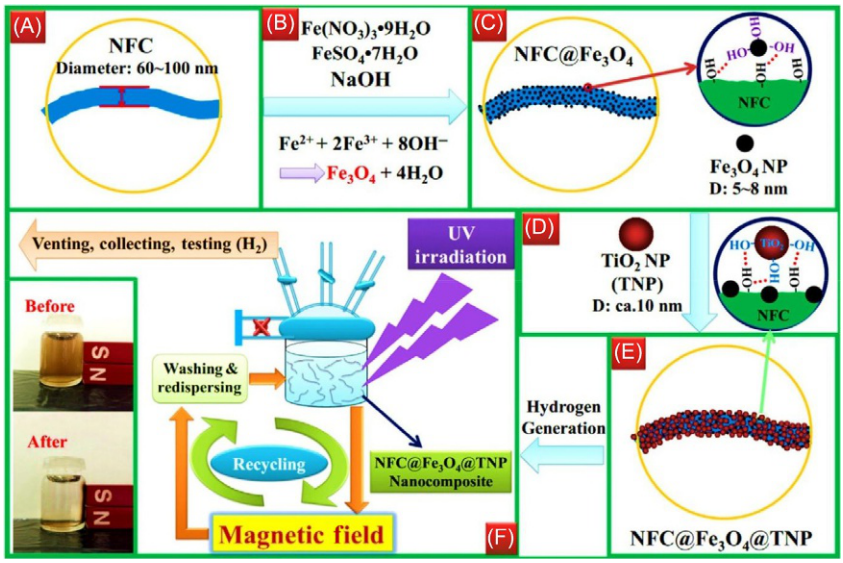

Fig. 13 Schematic representation for the preparation of NFC@Fe_3O_4@TNP NCs for photocatalytic hydrogen generation and recyclability; (A) NFC, (B) in situ preparation of Fe_3O_4 NP, (C) loaded Fe_3O_4 NP on the surface of NFC with hydrogen bonds, (D) adding dispersed TNP into as-prepared NFC@Fe_3O_4 NCs suspension, (E) loaded TNP on the surface of NFC@Fe_3O_4 NCs by hydrogen bonding with NFC, and (F) schematic of photocatalytic hydrogen generation and recyclability of NFC@Fe_3O_4@TNP NCs. *NFC*, nano-fibrillated cellulose; *TNP*, titanium dioxide nanoparticles; *NP*, nanoparticle; *NCs*, nanocomposites. *Adopted from X. An, D. Cheng, L. Dai, B. Wang, H.J. Ocampo, J. Nasrallah, X. Jia, J. Zou, Y. Long, Y. Ni, Synthesis of nano-fibrillated cellulose/magnetite/titanium dioxide (NFC@Fe_3O_4@TNP) nanocomposites and their application in the photocatalytic hydrogen generation, Appl. Catal. B Environ. 206 (2017) 53–64, with kind permission of Elsevier.*

5. Preparation of carbon nanomaterials/TiO_2 hybrids using ultrasonication

5.1 Graphene or graphene oxide/TiO_2 hybrids

As the hottest subjects in different domains like nanotechnology, chemistry, materials science, and physics, graphene, is an allotrope of carbon that is a honeycombed network of hexagonal rings of carbon. As recent studies, materials based on graphene have fascinated abundant attention in photocatalysis, photovoltaics, and electronics. Also, the oxidized shape of graphene is graphene oxide (GO), which has unique features and is a promising candidate in different fields [74, 75]. The researchers used these valuable compounds for the preparation of hybrid materials using TiO_2 particles. In the following, a number of examples are included with the applications.

Nuengmatcha et al. [76] reported the fabrication of ternary NC based on graphene, ZnO, and TiO_2 NPs as an efficient sono-catalyst for dye contaminants using ultrasonic waves. Moreover, the results were compared with the catalytic activities of its components (graphene, ZnO-graphene, and TiO_2). For the production of the sono-catalyst, at first ZnO/graphene composite was prepared with the addition of graphene oxide to $Zn(NO_3)_2$ $6H_2O$ solution under ultrasonication (2 h) and agitation (5 h). After heating at 600°C, ZnO/graphene was obtained. Also, colloidal TiO_2 solution was prepared with the dispersion of $C_{16}H_{36}O_4Ti$ in methanol employing ultrasound sono-reactor. Then, ZnO/graphene and TiO_2 solution were mixed and heated for removal of the methanol, and finally, the ZnO/graphene/TiO_2 NC was gained. The outcomes specified that ternary NC had higher activity compared to the other catalysts for degradation of dye pollutants and it presented greater sono-catalytic degradability for the MB in comparison to the other dye pollutants. In pH 9, 1.00 g/L of catalyst, 120 min irradiation time, 20 mg/L of dye, and 40% ultrasonic intensity, the best results were obtained. Hence this NC was a proper candidate for environmental uses. Fig. 14 shows a possible mechanism for

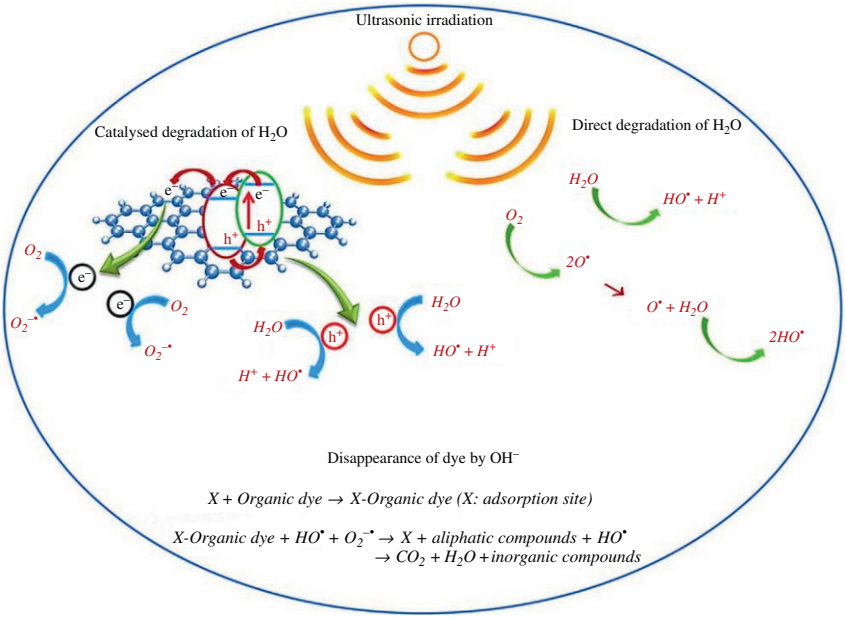

Fig. 14 Possible sonocatalytic degradation mechanism of ZGT catalyst on the degradation of organic dyes. *ZGT*, ZnO/graphene/TiO_2. *Adopted from P. Nuengmatcha, S. Chanthai, R. Mahachai, W.C. Oh, Sonocatalytic performance of ZnO/graphene/TiO_2 nanocomposite for degradation of dye pollutants (methylene blue, texbrite BAC-L, texbrite BBU-L and texbrite NFW-L) under ultrasonic irradiation, Dyes Pigments 134 (2016) 487–497, with kind permission of Elsevier.*

sono-catalytic degradation of dye under ultrasonication waves. Under ultrasonic irradiation, electrons and holes can be generated at NC surfaces, and react with hydroxyl ions and oxygen to produce radicals for dye molecule degradation.

In the study by Vajedi et al., [77] NCs based on reduced graphene oxide (rGO) and TiO_2 with 1:1, 1:0.1, and 0.1:1 mass ratios were successfully prepared by an eco-friendly and facile hydrothermal process using ultrasound. To this aim, GO, and TiO_2 were synthesized and distributed in DI water/ethanol by the assistance of ultrasonication and agitation with stirrer for the entire exfoliation of GO and homogenization of the suspension, respectively. Then, the as-prepared suspension was heated, centrifuged, washed, dried, and finally, the NCs were attained. The outcomes of analyses like UV-Vis, X-ray, BET, FE-SEM, and TEM, showed outstanding physical, optical, as well as electrochemical features. The fabricated NCs were applied as an effective adsorbent for elimination the Cd(II), Pb(II), as well as Cu(II) ions. Due to the wrinkled and squiggled structure of GO, good connections between TiO_2 NPs created and prevented them from aggregation and caused improvement in electrochemical performance for the metal ions adsorption. This work indicated that the NC comprising an equal amount of TiO_2 and rGO (1:1) was efficient and high sensitive adsorbent for heavy metal ions from solutions due to both properties of the TiO_2 and GO.

Also, Fausey et al. [78] prepared rGO-TiO_2@fiber NCs to remove arsenic contamination as hazardous matter in drinking water. Indeed, the profits of rGO-TiO_2 NCs and CS-based fibers were combined to improve the oxidation of arsenic. At first, nanofiber mats based on CS and poly(lactic-co-glycolic) were prepared via electrospinning procedure. Then, the fiber was enabled with rGO using bath-sonication. After that, TiO_2 was coated on GO@fibers, which for this purpose, TiO_2 was suspended in DI water with bath-sonication (10 min), GO@ fibers were added and mixed by orbital shaker as well as bath-sonication. After washing as well as drying, vitamin C was added for reduction of the GO on the surface of fibers and production of rGO-TiO_2@fiber. Surface morphology was studied with SEM analysis (Fig. 15). After bounding GO to the pristine fibers, GO sheets did not aggregate due to the epoxy-amine addition. With the TiO_2 addition, the particles can bind to GO and rGO, directly. The oxidative features of light irradiated rGO-TiO_2@fibers were compared with the non-reduced sample (GO-TiO_2-@fibers), and the outcomes showed that rGO-TiO_2@fibers oxidized As(III) ion 2.5 times more than the nonreduced sample. This improvement in oxidation by rGO-TiO_2-@fibers was due to the better conductivity of rGO in comparison with GO, permitting better shuttling of electrons away from the TiO_2's valence band and destruction of electron-hole recombination and raising the creation of OH radicals for oxidation of As(III) (Fig. 15).

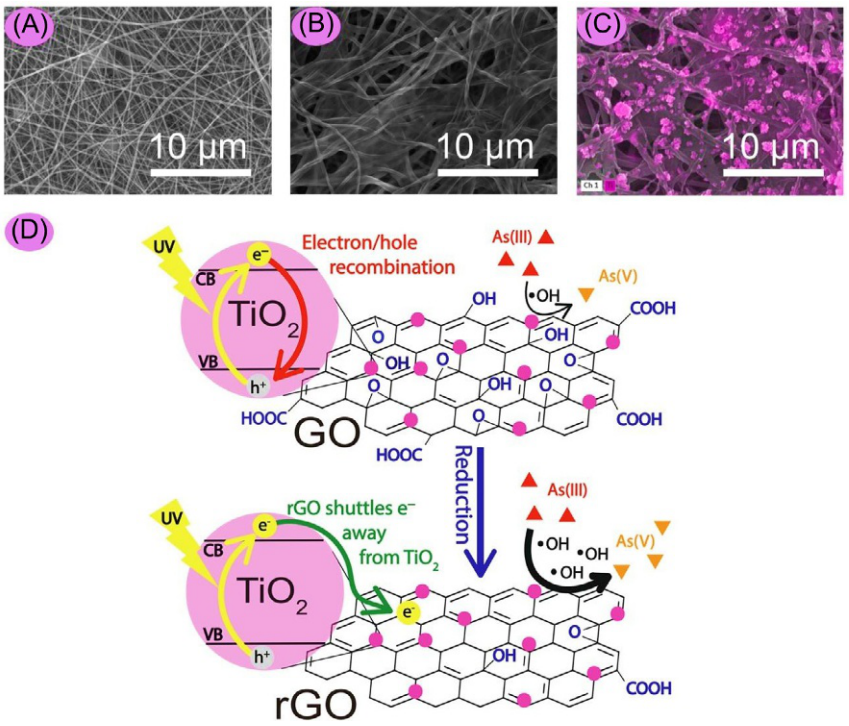

Fig. 15 Characteristics of GO and rGO-TiO_2 composite nanofibers. SEM images of (A) pristine fibers, (B) fibers coated with GO, and (C) fibers coated with rGO and TiO_2, and (D) Schematic illustrating the mechanism for enhanced synergy between rGO and TiO_2. Enhanced conductivity of rGO compared to GO allows increased shuttling of electrons away from TiO_2 throughout the rGO graphitic network, thereby suppressing electron-hole recombination and increasing the photocatlytic activity of TiO_2 bound to the rGO surface. *GO*, graphene-oxide; *rGO*, reduced GO. *Adopted from C.L. Fausey, I. Zucker, E. Shaulsky, J.B. Zimmerman, M. Elimelech, Removal of arsenic with reduced graphene oxide-TiO_2-enabled nanofibrous mats, Chem. Eng. J. 375 (2019) 122040, with kind permission of Elsevier.*

Harraz et al. [79] used ultrasonication for the fabrication of TiO_2/rGO NC through simple procedures in order to design and construct a highly selective and sensitive amperometric sensor for the vitamin C detection and determination with excellent action and reproducible behavior. To prepare the desire NC, first, GO was synthesized and distributed in water/ethanol solution via ultrasound to obtain GO suspension. Then, TTIP was added to this suspension and was ultrasonicated (60 min). After that, it was filtered and washed with ethanol and DI water. After heating at 450°C, the final product was attained. The as-prepared NC was fully characterized and the outcomes revealed the anatase phase of TiO_2 and wrinkled wave-like shape of GO. TiO_2/rGO NC was applied to modify the glassy carbon electrode. The sensor showed great performance due to the synergistic catalytic influence of high conductive rGO and semiconducting TiO_2 particles. Also, this sensor had unique selectivity, electrochemical stability, and repeatability.

Wu et al. [80] reported enhancement in antifouling and water flux performance of polymeric ultrafiltration membranes based on PVDF through introducing TiO_2/GO hybrid. At first, GO-TiO_2 NC was prepared through impregnation-precipitation. Then, by an ultrasonic probe, diverse amounts of TiO_2/GO were distributed in dimethylacetamide, and subsequently, PVDF and poly(ethylene glycol) (PEG) modifier were added, stirred, and finally cast on a glass plate. Owing to the interaction among GO and TiO_2, proper distribution of GO-TiO_2 happened. Porosity, pore size as well as surface hydrophilicity of the hybrid membranes increased; thus, antifouling and water flux enhanced. But in high amounts of TiO_2, agglomeration happened and subsequently, porosity reduced. Also, PEG acted as an additive for pore-forming, and it caused better porosity and hydrophilicity due to the enhanced distribution of TiO_2-GO in the polymeric membrane. Hence, membranes comprising PEG-modified TiO_2-GO displayed good performance.

In another study, TiO_2@rGO NCs were prepared via simple chemical method using ultrasonic irradiation for the enhancement of the photodegradation behavior of TiO_2 to eliminate the Rhodamine-B dye from a solution under UV light irradiation. The as-prepared TiO_2@rGO hybrid revealed an enhancement in photocatalytic actions for the elimination of dye. The achieved results indicated that, the highest dye elimination at pH 9, 60 min irradiation time, 0.3 g/L adsorbent, and 30 mg/L of dye concentration. Additionally, the results showing that by adding of rGO as an effective catalyst, photocatalytic behavior of TiO_2 was improved [81].

Alves research team [82], produced graphene/TiO_2 quantum dots by an oleothermal redox reaction of nano-emulsion of GO, TTIP, and oleylamine reductant for O_2 evolution reaction. Ultrasonic power was used to complete the dispersion of the GO in the oleic-surfactant and producing nano-emulsion. Temperature and reaction time influenced the crystallization and reduction ratio. When the temperature and reaction time increased, crystallization, as well as reduction of GO, promoted. Indeed, since one of the disadvantages of the usual hydrothermal production is the manufacture of agglomerated NPs, an innovative way to create spherically and well dispersed GO quantum dots from nano-emulsion was applied, and besides the utilization of this sample in the photo-electrochemical cell, it was obtained as a clear thin film.

Zhou et al. [83] invented rGO-TiO_2 NC via the one-step hydrothermal procedure and investigated the performance of it to remove humic acid as an organic pollutant. Ultrasonic waves were used to prepare a suspension containing GO with a better dispersion of the particles. The outcomes indicated partial reduction of GO to rGO in the hydrothermal production procedure, and uniformity of anatase TiO_2 growth on the rGO surfaces. Humic acid could be adsorbed onto the graphene surface owing to the outstanding conductivity and adsorption features of it. Due to the synergistic influence of functional groups on the surface and brilliant conductivity, rGO-TiO_2 NC revealed higher photocatalytic behavior. The effect of light intensity, NC amount,

and the temperature was investigated on the photocatalytic activity of the resulting NC. In pH 7, 4.37 W m^{-2} of light intensity, at 303 K, 1.2 g/L of NC, the maximum efficiency was achieved for the humic acid degradation.

Guo et al. [84] reported the use of ultrasonic waves in the hydrothermal method to fabricate rGO/TiO_2 NCs for degradation of quinolone antibiotics in wastewater. The characteristic outcomes demonstrated the successful production of rGO/TiO_2 NCs. The specific surface area of the NCs was larger than the pristine one. The manufactured NCs and pulsed discharge plasma (PDP) as one kind of progressive oxidation procedures, which apply for remediation systems, were coupled together in order to attain a synergetic influence to gain better performance, and the outcomes showed better degradation efficiency of PDP/rGO/TiO_2 (99.4%) than PDP and PDP-TiO_2 systems (64.8% and 75.7%, respectively). Also, antibiotic removal and kinetic constant were superior compared to the sole PDP.

Nasrollahzadeh reported [85] facile and green in situ synthesis of Ag NPs on GO/TiO_2 NC, for production of Ag/rGO/TiO_2 NC. Leaf extract of *E. helioscopia* L., which contains antioxidants, was selected as reductant and stabilizer for Ag^+ and GO reduction. At first, GO suspension was prepared via the dispersion of it in water with ultrasonic power. The TiO_2 particles were added and re-ultrasonicated to improve dispersion. $AgNO_3$ and plant extract were added to GO/TiO_2 NC and stirred, and finally, it was washed and dried. The GO/TiO_2 and Ag/rGO/TiO_2 NCs were characterized, and catalytic behavior of the obtained NCs for the reduction of nitrophenol and toxic dyes (Congo red as well as MB) was studied. The Ag/rGO/TiO_2 NCs was highly active and simply separated from reaction media through centrifugation. No significant deficiency in catalytic behavior was observed after several cycles.

Vinesh et al. [86] prepared Au/boron-TiO_2/rGO hybrid through the modest hydrothermal process to degrade tetracycline antibiotics under ultrasound waves. Insertion of boron, as electron-deficient atom, which could form acceptor energy level, and the existence of Au plasmonic metal as cocatalyst improved optical absorption of TiO_2 in the attendance of rGO support. For the preparation of Au/boron-TiO_2/rGO, briefly, boric acid, $AuCl_3$, and TTIP were stirred for mix together. Meanwhile, GO solution was prepared by dispersing it in water with sonication power in an ultrasonic bath. Then, GO suspension was added to the mixture and was stirred. After centrifugation, washing, and drying, the product was gained. Based on the outcomes, due to the synergic effect of manufacturer constituents, this fabricated photocatalyst enhanced the degradation rate of tetracycline. Indeed, ultrasound forces and boron atom, as well as rGO support facilitated the separation of electron-hole pair ultrasound forces and degradation activity increased.

Park et al. [87] used ultrasonic spray pyrolysis as a simple method for the preparation of rGO/TiO_2. The fabricated hybrid applied for the MB degradation. Indeed ultrasonic spray pyrolysis inhibited the TiO_2 aggregation and improved the photocatalytic behavior of the hybrid. The rGO/TiO_2 hybrids had better photocatalytic performance than TiO_2

and degraded MB, effectively. Fig. 16A and B exhibit the SEM photographs for the TiO_2 with a spherical shape, and rGO/TiO_2 hybrids with crumpled shape. Fig. 16C and D displays TEM images of the samples, respectively. Based on outcomes, ultrasonic spray pyrolysis distributed the nano-TiO_2 homogeneously on the graphene lattice. Fig. 16E shows a graphic design for the fabrication of the rGO/TiO_2 with ultrasonic spray pyrolysis method.

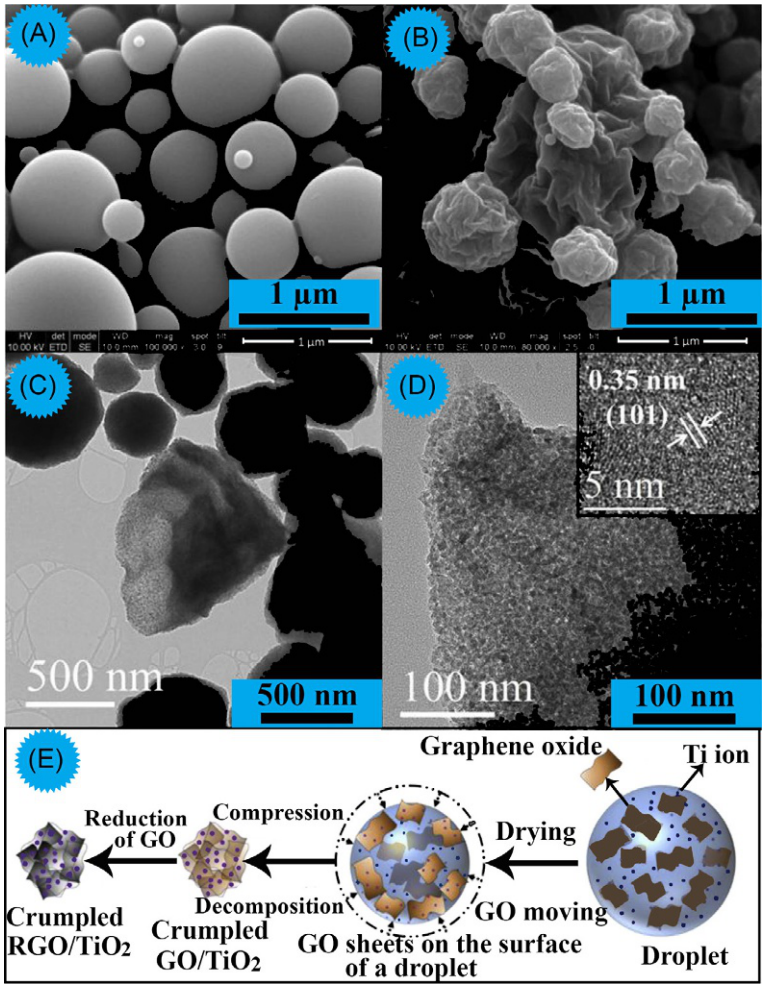

Fig. 16 Morphology of samples prepared by ultrasonic spray pyrolysis; SEM images: (A) bare TiO_2 and (B) RGO_5/TiO_2, HRTEM images: (C) low magnification, and (D) high magnification of RGO_5/TiO_2, and (E) schematic illustration showing the formation of RGO/TiO_2 composite during ultrasonic spray pyrolysis. *HRTEM*, high-resolution transmission electron microscopy. *Adopted from J.A. Park, B. Yang, J. Lee, I.G. Kim, J.H. Kim, J.W. Choi, H.D. Park, I.W. Nah, S.H. Lee, Ultrasonic spray pyrolysis synthesis of reduced graphene oxide/anatase TiO_2 composite and its application in the photocatalytic degradation of methylene blue in water, Chemosphere 191 (2018) 738–746, with kind permission of Elsevier.*

5.2 Carbon nanotubes (CNTs)/TiO_2 hybrids

As multipurpose elements in the whole world, carbon atoms can be arranged in different forms. CNTs, as fullerenes family members with a cylindrical shape, have excellent features like great area, thermal, and chemical stability. They can be used in therapeutic utilizations like cancer therapy, gas-sensors, electronics, remediation industry, NCs, and so on [88–91]. Numerous NCs based on CNTs and TiO_2 were reported, which many of them are mentioned as follows:

Lithium-sulfur batteries are considered as energy storage systems because of low toxicity, reasonable price, and abundance of sulfur. But, owing to the undesirable shuttle influence from polysulfide and to develop the act of Li-S battery, Li et al. [92] invented a new polysulfide barrier layer comprised of mesoporous TiO_2 and CNT. Indeed, in order to limit the migration of polysulfides, TiO_2 particles and CNTs were used because of good absorption ability of titania and threaded structure of CNTs as a collector for reusing the trapped polysulfides through TiO_2 particles. In order to prepare the mesoporous TiO_2-CNTs interlayer, ultrasonic treatment was used to disperse and homogenize the materials for better performance. Due to the existence and combination of CNTs and TiO_2 networks, electrochemical performances of batteries were enhanced. The structure of a prepared lithium-sulfur battery employing TiO_2-CNTs is demonstrated in Fig. 17A. Due to the flexibility of CNTs in the attained membrane displayed outstanding mechanical features like good flexibility and strength (Fig. 17B). Fig. 17C shows cross-section microscopic image that indicates membrane thickness is about 8 mm. Fig. 17D and E shows a string structure of TiO_2 that looks like a pearl necklace threaded structure of CNTs.

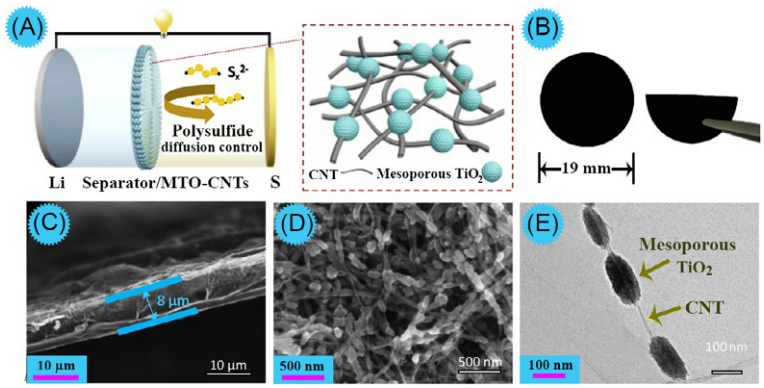

Fig. 17 Schematic cell configuration of Li-S batteries using MTO-CNTs interlayer. (A) Optical photographs, (B) cross-section, (C) top-down SEM images of the MTO-CNTs interlayer. TEM images at (D) low and (E) high magnification of the MTO-CNTs. *MTO*, mesoporous TiO_2; *CNTs*, carbon nanotubes. *Adopted from N. Li, Z. Chen, F. Chen, G. Hu, S. Wang, Z. Sun, X. Sun, F. Li, From interlayer to lightweight capping layer: rational design of mesoporous TiO_2 threaded with CNTs for advanced Li–S batteries, Carbon 143 (2019) 523–530, with kind permission of Elsevier.*

Ghartavol et al. [93] prepared solar cells sensitive to dye, based on nano-TiO_2 photoanodes, which were decorated by CNT/TiO_2 composite. In order to manufacture the CNT/TiO_2 hybrid, CNTs were dispersed in ethanol using ultrasonication waves for separation of the bundles, then, DI water and benzyl alcohol were added and stirred. TTIP solution was dropped in it slowly and subsequently stirred, filtered, washed, and dried. The CNT/TiO_2 core-shell was characterized by several techniques. Morphological examinations exhibited TiO_2 formation as a shell on CNT surfaces as the core. Based on outcomes, by incorporating the CNT/TiO_2 core-shell, power conversion efficiency of solar cells enhanced up to 37%.

Zolfaghari-Isavandi research team [94], functionalized CNTs and then prepared CNTs/TiO_2 NCs comprising several amounts of CNTs and as photoanode pastes in solar cells application. In the preparation strategy of TiO_2/CNT NCs, ultrasonic irradiation was applied for dispersion of CNTs in a solution containing TiO_2 paste. The outcomes indicated improvement in CdS solar cells with the aid of TiO_2/CNT photoanode.

Zhu et al. [95] employed an ultrasound-assisted technique for synthesizing Ag_2S-TiO_2/CNT NCs. The surface state, microstructure, as well as elemental combinations of the fabricated NCs, were examined by many techniques. The photocatalytic behavior of the Ag_2S-TiO_2/CNT NCs was evaluated by investigating the Rhodamine B degradation. In addition to the kinetics, photocatalysis mechanism of the NCs was examined. Based on the charge transfer manner and excitation patterns among TiO_2, Ag_2S, and CNTs, electrons and holes were created and after migration to the conduction and valence bands, radicals for the degradation purpose were produced. The fabricated NCs revealed higher photocatalytic behavior than pristine TiO_2 due to the CNT network.

Hemmat Esfe et al. [96] investigated the dynamic viscosity of many nano-lubricant containing diverse combinations of TiO_2 NPs and CNTs in engine oil. The significant result of this study was the influence of CNT on the rheological performance of nano-fluid. In order to achieve the nano-fluid, oil was added to the mixture of nanomaterials and was blended via stirrer. Afterward, ultrasonic homogenizer was used to prepare the homogenous suspension. The influence of the shear rate and temperature was examined. With increasing temperature, viscosity was reduced (about 80%). Also, in a larger amount of CNT, nano-fluid showed the non-Newtonian performance.

Jayanthi Kalaivani et al. [97] incorporated TiO_2 into the paste matrix for the development of a sensitive enzymatic biosensor. Inulin, as electroactive carbohydrate, was used to prepare the Inulin/TiO_2 composite. Ultrasonic waves were employed for dispersion of TiO_2 NPs in the Inulin matrix. In order to enhance the biocompatibility, stability, and hydrophilicity of CNT; the fabricated Inulin/TiO_2 composite was employed for CNTs modification. Many techniques were employed for characterization of the CNT/Inulin-TiO_2 bio-NC. The invented biosensor presented good selectivity, sensitivity, as well as stability.

Kumar et al. [98] decorated TiO_2 NPs on the CNT surface and fabricated CNT/TiO_2 hybrid structure as filler for reinforcement in an epoxy matrix. Ultrasonic cavitation was used for decoration of CNT and preparation of epoxy NC. To decorate the CNTs with TiO_2 particles, CNTs, and TiO_2 NPs were sonicated, stirred, and finally dried. Afterward, this hybrid was mixed with epoxy resin by glass rod stirring and ultrasonic waves for the better dispersion of the filler in the matrix. Morphological studies indicated superior dispersion of CNT/TiO_2 filler in epoxy, mechanical as well as anticorrosion features were tested and the outcomes revealed superior mechanical performance (like storage modulus and tensile strength), and anticorrosion feature.

6. Conclusions and future prospects

Sonochemistry, as a green technology in innovation, is used in various fields like organic synthesis and surface modification of metal oxides, as well as the construction of different polymeric NCs for usages in numerous areas like environmental remediation, packaging, textile, and so on. Indeed, sonochemistry has many advantages in comparison with the conventional techniques, simple equipment decreases in time, waste production, and energy. These benefits encourage chemists and other scientists in multidisciplinary research and development to apply sonochemistry and progress different utilizations based on the ultrasound. In this chapter, we presented the organo-synthesis of materials based on TiO_2 metal oxide through the sonochemical method. Meanwhile, diverse utilizations for the obtained hybrids were mentioned. They may have different applications like in packaging, textile, and heavy metal or dyes adsorption. Furthermore, some of the advantages, as well as disadvantages, were offered. At last, but not least in order to avoid wasting time, energy, and environmental problems, it is recommended to pay more attention to this technology for the future investigations in the research and development from academia as well as industrial point of view.

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CHAPTER 12

Sonochemical protocol of polymer synthesis

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1. Emulsion polymerization

An individual method which applied for several radical chain polymerizations is called emulsion polymerization that monomers polymerize in the appearance of emulsions (i.e., colloidal dispersions). The method of emulsion polymerization has some advantages which can be listed as follow:

- The ease of process control resulting from the condition of the emulsion approach.
- As compared to bulk polymerization, the problems associated with temperature and viscosity are much less significant.
- *Latex* as the produce of an emulsion polymerization is applied in the absence of further treatments [1].

As of now, we can assume that the rate and speed of emulsion polymerizations can be accelerated by ultrasonic irradiation. This acceleration is the result of the following two properties of irradiation which are explained as follows:

- Degassing effect of ultrasonic cavitation;

Causes the oxygen to deploy efficiently from reactants causing the transfer reactions to be less possible, which shortens the induction period and thus leads to a higher polymerization rate.

- Ultrasound cavitation causes a localized heating of the reaction medium [2].

As explained for emulsion polymerization, ultrasonic-assisted emulsion polymerization comparing common emulsion polymerization has the following advantages as an example;

- Absence of chemical initiators
- Rapid polymerizations
- Production of nanosized latex particles
- Production of polymers with high molecular weights [3].

Ultrasound is an initiator which causes chemical linkages of molecules to be broken, and hence the rate of polymerization enhances, which can be used in extreme states created through acoustic cavitation in the area of polymer science [1]. Ostroski and Stambaugh explained the significant acceleration of a conventional emulsion polymerization using

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the sonication method in the 1950s. It was concluded that ultrasonic induced agitation will result in a faster and improved emulsification stemming which was caused because of the increased decomposition of the chemical initiator in aqueous solutions.

Ultrasound as an initiator for the polymerization of acrylonitrile was first used in early 1951. To this day, researchers have been mostly concerned with the homopolymerization of a monomer in a good solvent, and pure monomer melt [3].

Kruus and Patraboy, with the help of intense ultrasound, have done the polymerization initiation of methyl methacrylate monomer in a solution of vinyl monomer [4].

The final latexes with diameters of 50 nm were produced under ultrasonic irradiation in the polymerization of styrene in aqueous medium emulsion, in the absence of an initiator, which was conducted at 30°C. The molecular weights of polystyrene were high ($>10^6$). Ultrasonic initiation is an alternative process for the synthesis of small latex particles. This process requires low levels of surfactants as stabilizers for emulsion polymerization [2].

Moreover, Cheung and Gaddam studied the effects of ultrasound on methyl methacrylate and styrene emulsion polymerization. At different temperatures, they used Azobisisobutyronitrile and Potassium persulfate as initiators. They reported a higher polymerization rate at low temperatures (50°C) under ultrasound treatment. They also reported that ultrasound at higher temperatures (70°C) does not affect the polymerization rate. Thus, reaction temperature is a key during the polymerization assisting with the ultrasound. High vapor pressure, which is the result of higher temperatures, guides to the formation of a fewer amount of radicals due to less intense cavity collapse. These radicals are required for polymerization to be initiated. Therefore, for energy saving, ultrasound is used in emulsion polymerization at lower temperatures [5]. As an example, *n*-butyl acrylate emulsion polymerization assisting with ultrasound initiation without using a chemical initiator has been investigated. The obtained results showed that high evaluation of *n*-butyl acrylate through a high ejection rate of N_2 can be achieved in a shorter time if the ultrasonic method is employed [6].

In another investigation, the factors deciding the rates of ultrasound-assisted initiated polymerization of various methylacrylate monomers were studied. The procedure of these chemical reactions was according to pseudo-first-order kinetics as indicated by the results. Pseudo-first-order kinetics confirms the utilization of a zero-one model such that pseudo-instantaneous termination occurs by entering a radical to a particle including a rising radical for polymerization. The polymerization rate of monomers, as indicated by the experimental results, is related to the variances in the monomers surface operations [7].

Fig. 1 shows the general process of the macromolecule latex's preparation, as proposed by Bradley and Grieser. In short, dispersion of monomer droplets in the aqueous phase is achieved *via* the efficacy of the cavitation process. The stabilization of these

droplets is done through the adsorption of surfactant molecules on the monomer droplet/water interface. The acoustic cavitation process generates primary radicals ($^{\bullet}H$ and $^{\bullet}OH$) which release a monomer droplet directly and cause the initiation of the polymerization reaction within a droplet. Or these radicals can interact with the monomer structures adsorbed to the interface of the cavitation bubble/solution and create monomeric radicals, which can cause the same direct diffusion to a monomer droplet and start the polymerization reaction. Therefore, the droplet of monomer is polymerized, and eventually a latex particle is formed [8, 9].

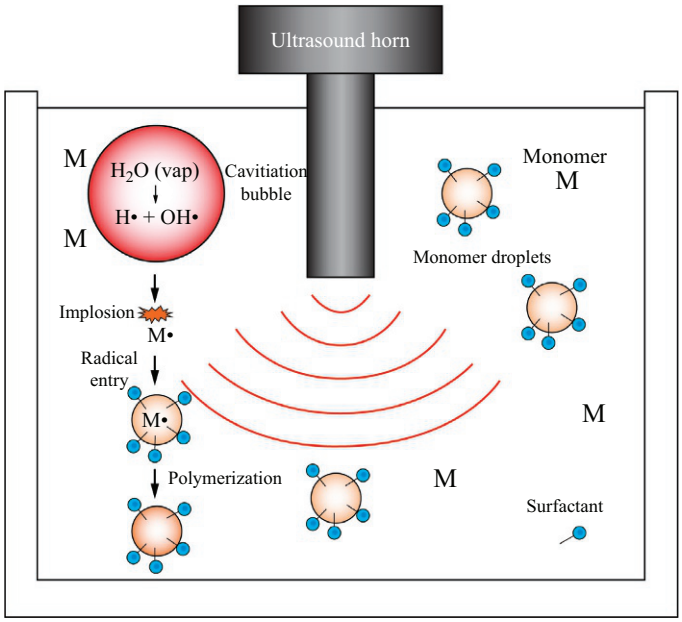


Fig. 1 Schematic diagram of the proposed emulsion polymerization process induced by ultrasound [8].

In an ambient atmosphere, by the usage of ultrasonic energy the emulsion polymerization of vinyl acetate can be initiated. This process (ultrasonic power plus a redox initiator) will result in a better and sufficient polymerization rate in which directing the particle size and molecular weight of vinyl acetate polymer is possible. Ultrasonic-assisted polymerization also generates a steady, milky white, dirty emulsion of vinyl acetate [10].

1.1 Ultrasound-assisted mini-emulsion polymerization system

The polymerization of poly(methyl methacrylate) and poly(butyl acrylate) by ultrasound in the presence of dodecyl trimethylammonium chloride as a cationic surfactant has

shown considerable changes in the polymerization rate. At 30°C, stable dispersions with a diameter of 40–150 nm and polymer molecular weight of 106 g mol^{-1} are formed in the polymerization of mixed oil-in-water emulsions of monomeric forms, which was an initiator-free reaction. An ionic surface active agent as straightener will cause the creation of clear latex particles [6]. The obtained results reveal a mini-emulsion method, in which nucleation of particles continually occurs in the reactions of a monomer to polymer changing [9].

Under ambient conditions, the mini-emulsion polymerization of *n*-butyl methacrylate (BMA)-assisted with ultrasound using the mixtures of aliphatic and aromatic hydrocarbon liquids-is investigated to measure the monomer transformation percent and molecular weights of the BMA macromolecules. Also, the kinetics of the polymerization practice and resultant polymer features according to these measurements is studied. The results showed that the polymerization rate and molecular weights of the polymers were influenced by the nature of the organic liquid existent in the emulsion and its share in mixture content. As the experiments showed, there were no significant changes when using aliphatic organic liquids in the rates of BMA polymerization, whereas in the case of aromatic liquids a considerable reduction of the polymerization rate and decrease in polymer size were observed. Chain transfer reactions and creation of a radical complex among the propagating radical and the organic liquid in the oil blend effect the kinetics of the polymerization practice [11].

Further, the effect of free radicals in semibatch miniemulsion was studied wherein ultrasound and an external addition of initiator is used to produce free radicals. The effect of different reaction conditions was also reported in the literatures [7].

1.2 Ultrasonic initiation of aliphatic alcohols polymerization

Aliphatic alcohols as hydroxyl radical trappers increase the polymerization rate of ultrasonically initiated emulsion polymerization since these alcohols can release into cavitation bubbles and interact with $^{\bullet}OH$ produced by the sonolysis of water, which can produce hydroxyalkyl radicals. Increasing the reaction system radicals is proved by the measurements of H_2O_2 yield and the rate of polymerization at the various aliphatic alcohols. For example, using methanol as one of these aliphatic alcohols will result in the following phenomena:

- Scavenge $^{\bullet}OH$ to enhance the content of radicals
- Quench ultrasonic cavitation

The high temperature and high pressure result in the drop in the content of radicals which will reduce the polymerization rates. Methanol, by decreasing the ultrasonic cavitation temperature and pressure, causes the reaction to continue efficiently. In this case, it includes two reactions which affect the initialization of the polymerization and decides the optimized concentration which will have the fastest reaction rates (Fig. 2) [12].

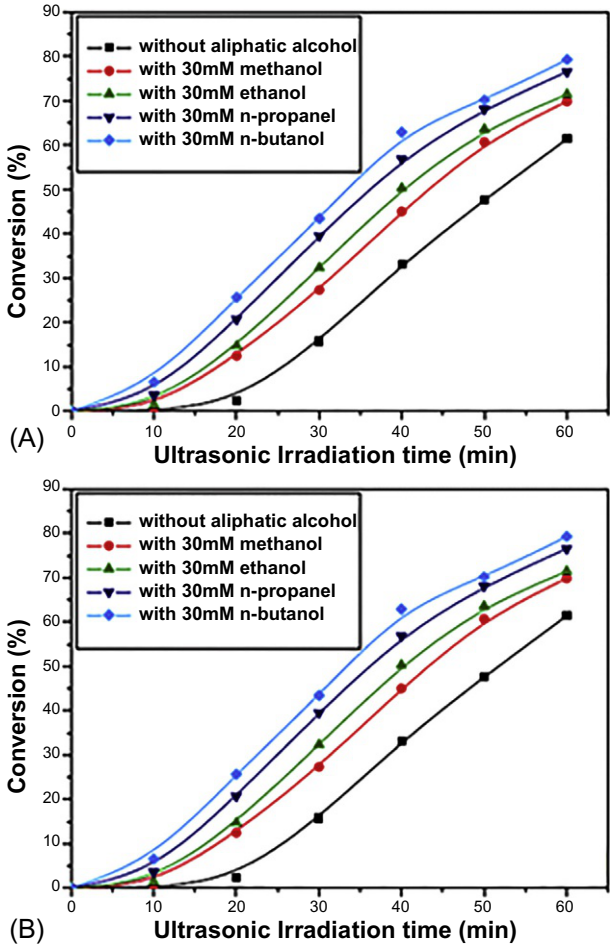


Fig. 2 (A) Conversions-ultrasonic irradiation time curves of ultrasonically initiated emulsion polymerization of styrene in the presence of various aliphatic alcohols. (B) Conversion-ultrasonic irradiation time curves with different amounts of methanol [12].

1.3 Liquid carbon dioxide systems

Ultrasound is used in the high-pressure liquid carbon dioxide systems. MMA-CO_2 and styrene-CO_2 medium have been the subjects of both polymerization and radical scavenger detection studies. UV-vis analysis determined the radical formation rate and the cavitation has been proven by the results. As mentioned before, the irradiation period (ultrasonic process) has a considerable impact on the molecular weight and its dispersal in a polymer. Also, the ratio of CO_2/monomer content has an influence on the molecular weight dispersion confirmed by the outcomes obtained from the polymerization process. A comparison of the SEM images revealed that ultrasound irradiation causes the steady

distribution polymerization in liquid CO_2, which proves that this polymerization can efficiently do without using a stabilizer. A handmade reactor was used for the purposes of this research. It is a cylindrical reactor with a 45-mL capacity, manufactured from stainless steel. Fig. 3 is a schematic illustration of the experiment. Two tempered steam gauge glass windows was equipped to the cell until detect the cavitation experience [13].

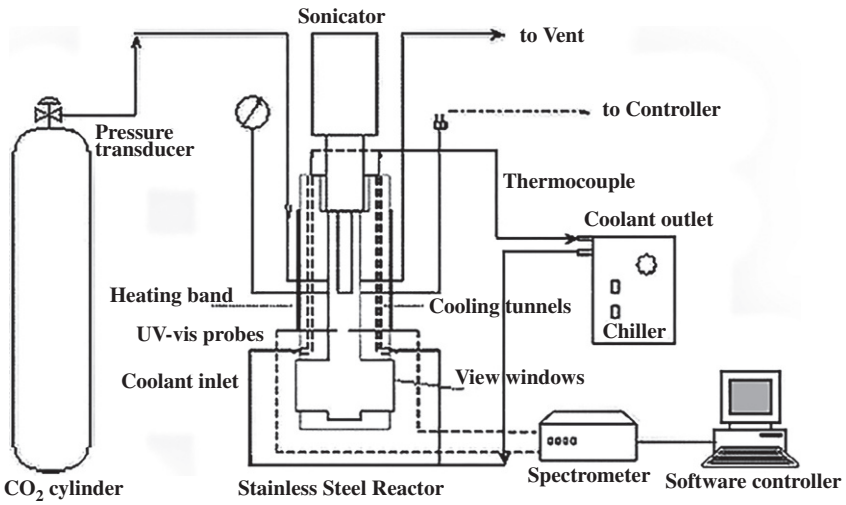


Fig. 3 Schematic representation of the experimental apparatus [13].

1.4 Indirect ultrasound-assisted emulsion polymerization

Frequency and the reactor's situation influenced the polymer yield and molecular weight of the produced polymer under indirect ultrasonic irradiation. The irradiation process is carried out in three stages and the effects of ultrasound on polymerization were investigated. It was concluded that, by the creation of a steady emulsion in the first step and changing the frequency of the sound and reactor's position in a parallel process with irradiation time in the next two stages, an improvement in polymer yield can be expected. Also, the molecular weight of the polymer was with altering the reactor's situation with irradiation in two steps was controlled, which in the second stage maintained low chain scission energy. This dynamic process, which includes the changes in irradiation manner over the way of the polymerization, is an effective application to intensify the emulsion polymerization practice. The complete experimental procedure is explained in Fig. 4. The temperature of the water bath was preserved steady at 30°C by a thermostatic stream of water. The nitrogen was constantly flowing through the reaction because of the gas needed for the ultrasound started emulsion polymerization of MMA [14].

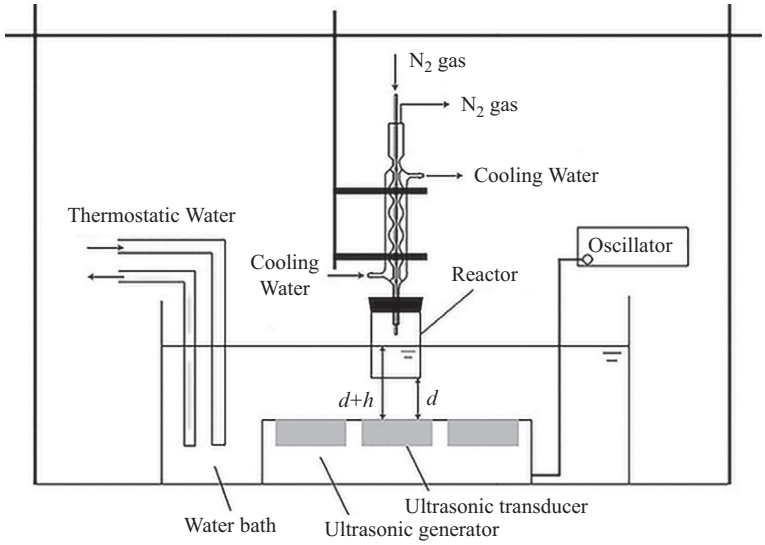


Fig. 4 Experimental setup [14].

1.5 Ultrasound-assisted emulsion polymerization to produce hydrogel polymer

The in situ emulsion polymerization of the three component system as a poly(acrylic acid)-bentonite-FeCo hydrogel nanocomposite *via* ultrasound is investigated. The physical properties of hydrogel are improved with the addition of delaminated bentonite clay sheets and the use of Fe-Co helped the adsorption of an organic pollutant [15].

1.6 Ultrasound-assisted emulsion copolymerization of butyl acrylate/vinyl acetate

As in the meaning of it, two different respiting units form a copolymer. Thus, the copolymerization process involves a simultaneous polymerization of two different monomers to form a single polymer chain [1].

Emulsion of butyl acrylate and vinyl acetate has been reacted under ultrasonic and without any added initiator. In this method, ultrasonic cavitation formed the radicals required for the polymerization. The kinetic studies of the reaction revealed that the polymerization rate at equivalent monomer concentrations of vinyl acetate have markedly lower values when compared to the butyl acrylate. The numbers of particle sizes and polymer molecular weight confirm that the monomer evaporation into the

cavities resulted from ultrasound effect, dampening the cavitation process to result in a lower radical density [16]. At higher ultrasonic power, the time of the reaction was shortened and the monomer conversion was at its highest level. These factor resulted in a diminution in the average molecular weight [17].

1.7 Ultrasound-assisted graft copolymerization of acrylic acid/poly (vinylidene fluoride)

Grafted Acrylic acid (AA) to the hollow fiber membrane of poly(vinylidene fluoride) (PVDF) was prepared by the ultrasound-assisted graft polymerization method (Fig. 5). In general, the attaching compactness improved with the rise of ultrasonic power, but the enhancement in the rate of the polymerization at the beginning was higher and the rate becomes lower as the reaction proceeds (Fig. 6B) in a way that, at an ultrasonic power of 1080 W, the attaching density had a steady value and no change was reported [18].

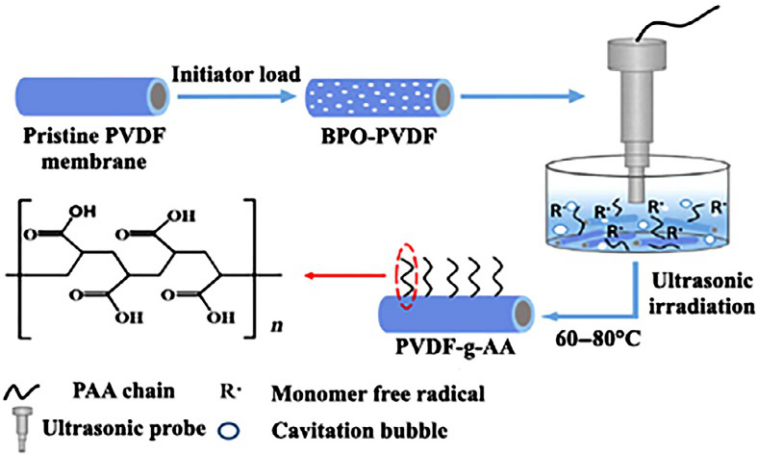


Fig. 5 Schematic representation of the modification process of PVDF hollow fiber membrane using AA as the graft monomer [18].

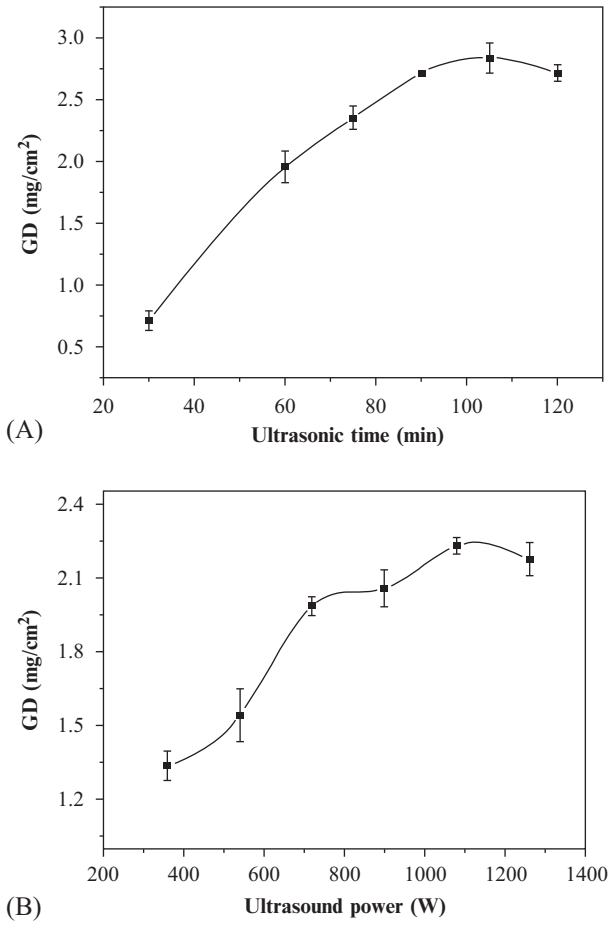


Fig. 6 Graft dispersity versus different conditions: (A) ultrasonic time, and (B) ultrasonic power [18].

1.8 Ultrasonic-assisted emulsion polymerization of polyaniline/nanostructure TiO_2 nanocomposites

Encapsulation or surface grafting of nano inorganic additives and polymers has been employed to produce polymer nanocomposites [19]. Various methods such as intercalative polymerization, suspension polymerization, emulsion polymerization, etc. are employed in the fabrication of nanocomposites [20, 21]. Along with these methodologies, ultrasonic irradiation was used to prepare some desired environment and effects in order to achieve a better dispersion of the nanocomposite component [22–26]. For example, the polymerization of polyaniline/nanostructure TiO_2 nanocomposite particles under ultrasonic was studied. Ultrasonic can reduce the assortment of nano TiO_2

particles, and so the nanoparticles are prepared accordingly to be dispersed in aqueous solution. Deposition of polyaniline on the surface of the nanoparticle will produce a core-shell form. In this process, conductivity of the samples increases when ultrasonic irradiation is used. Therefore, when the polyaniline content declines to ~10%, the conductivity of the nanocomposite stays intact at 10^{-1} S cm^{-1} (Fig. 7) [27].

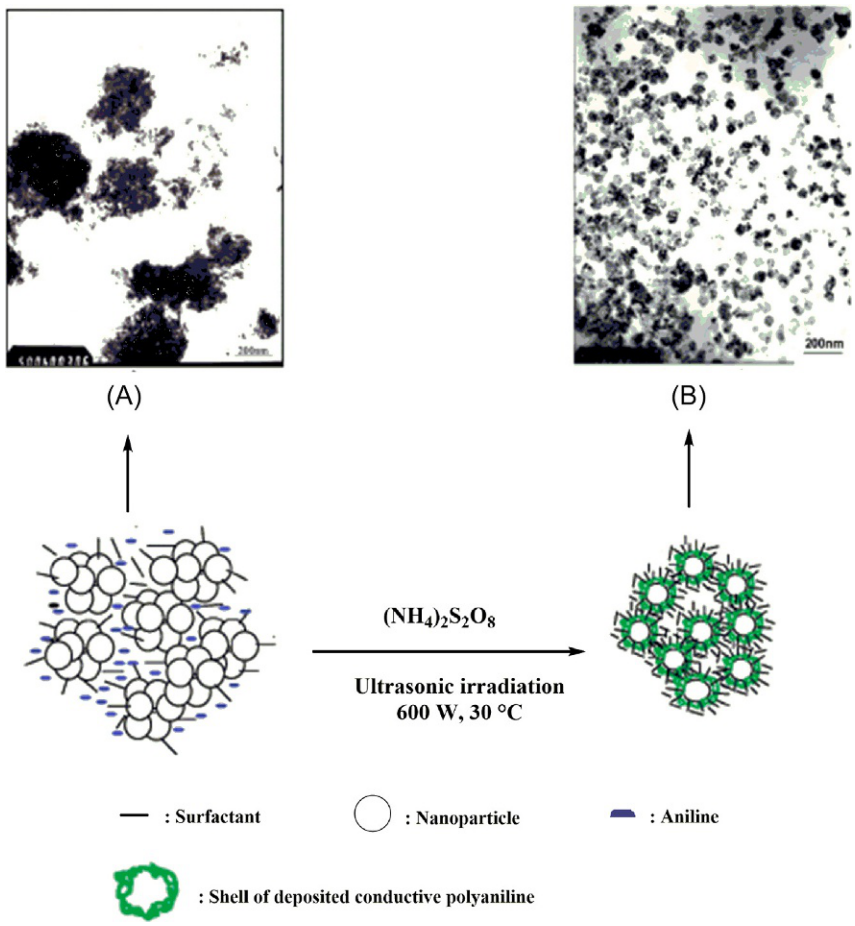


Fig. 7 Formation of core-shell polyaniline/nanocrystalline TiO_2 composite particles: (A) TEM photograph of aggregates of nanocrystalline TiO_2 in aqueous solution; (B) TEM photograph of polyaniline/nanocrystalline TiO_2 composites particles obtained through ultrasonic irradiation [27].

1.9 Ultrasound-assisted emulsion polymerization ZnO/poly(butyl methacrylate) nanocomposites

In another approach using the hydrothermal-sonochemical emulsion polymerization technique, zinc oxide (ZnO)/poly(butyl methacrylate) (PBMA) and PBMA/polyaniline (PANI)-ZnO latex nanocomposite were synthesized. This study had three main objectives:

(1) Synthesis of modified ZnO nanoparticles by sonochemistry
(2) ZnO-PBMA synthesis by sonochemical emulsion polymerization in green media
(3) Enhancing the properties of ZnO-PBMA latex for anticorrosive applications [28].

1.10 Ultrasound-assisted emulsion polymerization of the poly (styrene-*co*-methyl methacrylate)/montmorillonite nanocomposite

The ultrasonic-assisted emulsion copolymerization of styrene and methyl methacrylate is studied. It has been observed that the ultrasound in the synthesis of the exfoliated structure poly (styrene-*co*-methyl methacrylate)/exfoliated montmorillonite (P(MMA-*co*-St)/O-MMT) nanocomposite lowers (at a fivefold faster polymerization rate) the time required for the polymerization to take place, along with the higher polymerization rate and better distribution of MMT in polymer latex. Fig. 8 is a schematic illustration of the exfoliated P(MMA-*co*-St)/OMMT nanocomposite synthesis mechanism. The first stage shows the mixing of O-MMT with styrene in the existence of the ultrasonic wave to create the exfoliated structure. Ultrasound and its cavitation effects create high shear levels that, related to strong confusion, will result in clay domination into single sheets, which make easier the dispersion of these platelets into the monomer phase. In the second stage, the polar carboxyl groups of the methyl acrylate and styrene react by the polar groups (−OH) existing on clay sheets leading to an establishment of steady emulsion droplets of monomers. Ultrasonic irradiations create the implosion of cavities, which is one of the reasons for the formation of the radicals throughout the polymerization process. This radical generation quantity also decreased the distribution resistance resulting from unstable conditions caused by the cavitational factors of ultrasonic, which will result in much faster polymerization rates. The diffusion resistance reduction increases the micro-vortex sign of the component, causing great effects in the reaction condition [29].

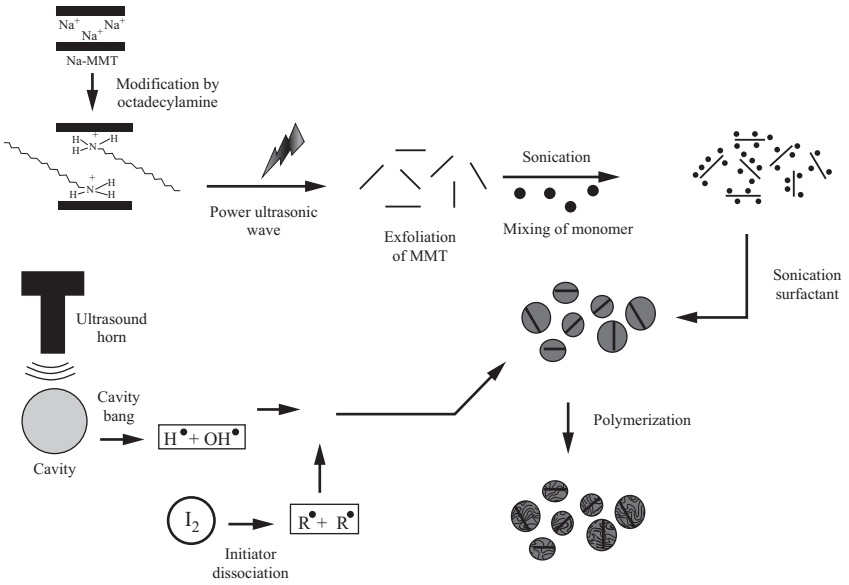


Fig. 8 Schematic mechanism for exfoliation of MMT and the formation process of P(MMA-*co*-St)/O-MMT nanocomposite [29].

1.11 Ultrasound-assisted mini-emulsion production of polypyrrole-ZnO (PPy/ZnO)

Oil-water mini-emulsion synthesis of PPy/ZnO by ultrasound was investigated. As was evident by the TEM images, uniform dispersion of ZnO nanoparticles in the polypyrrole medium was achieved due to the influence of ultrasonic energy on the polymerization medium. Ultrasound controlling the sizes of the particles improves the cooperation between ZnO and PPy nanoparticles. Fig. 9 demonstrates the reaction mechanism of a hybrid PPy/ZnO nanocomposite formation in the presence of ultrasound. As is obvious in Fig. 9, ultrasound produces cavitation conditions which are responsible for the creation of a mini-emulsion. Also, high temperature and pressure in the bubbles and intense shear energy in the medium are the results of the crumble in cavitation bubbles. Such forces can prepare such conditions prior to the uniform decomposition of ferric chloride into iron (ferric) and chloride ions and the production of identical and nanosized droplets. Furthermore, the shock waves of ultrasound cavitation caused destruction of the particles. This fragmentation breaks the particle aggregation, thus resulting in superior control over the size dispersal. Ultimately, the produced PPy/ZnO hybrid nanocomposite is stabilized with the surfactant SDBS. Py is the pyrrole monomer, and Py^+ is the radical cation which can dimerize by the elimination of H^+ with ultrasound, such as given below in reactions (1)–(4): [30]

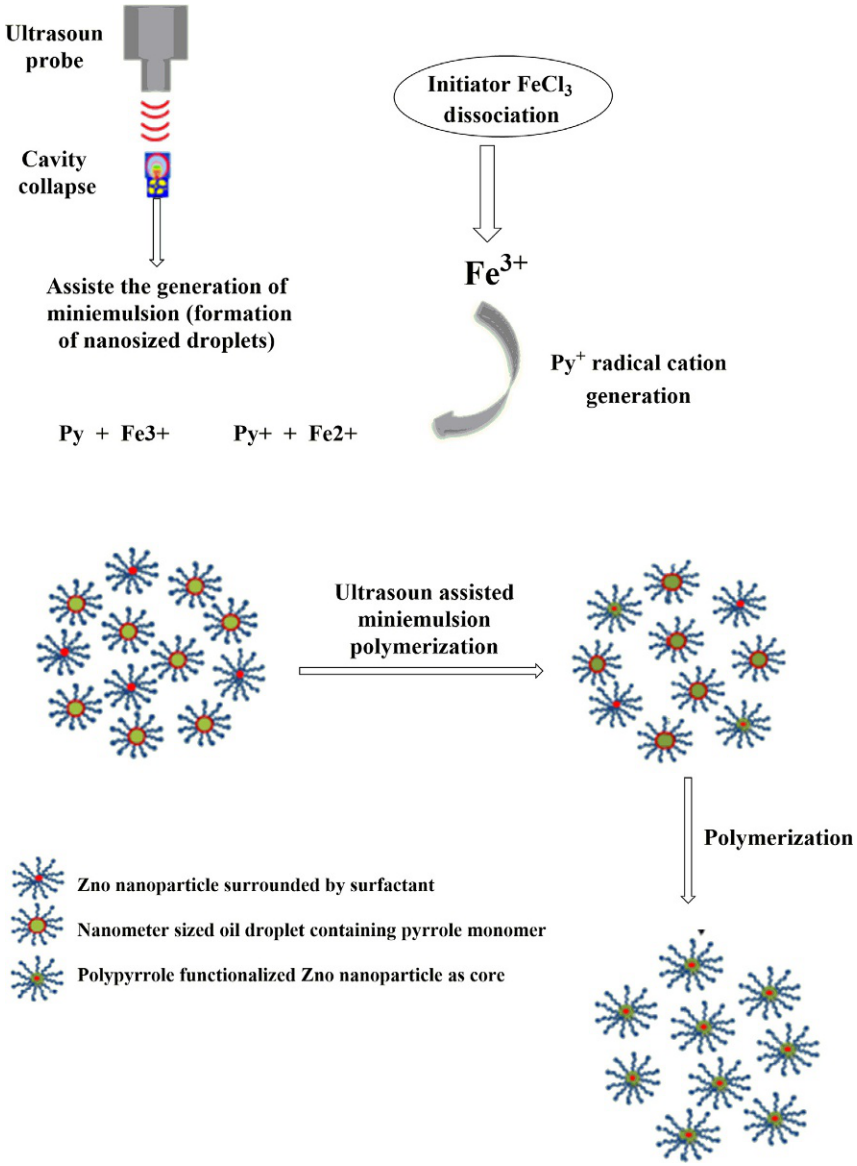


Fig. 9 Mechanism of functionalization of ZnO nanoparticles using polypyrrole in the presence of ultrasound during miniemulsion polymerization [30].

$$\mathrm{Py} + \mathrm{Fe}^{3+} \rightarrow \mathrm{Py}^{+} + \mathrm{Fe}^{2+} \tag{1}$$

$$2\mathrm{Py}^{+} \rightarrow \mathrm{Py} - \mathrm{Py} + 2\mathrm{H}^{+} \tag{2}$$

$$\mathrm{Py} - \mathrm{Py} + \mathrm{Fe}^{3+} \rightarrow \mathrm{Py} - \mathrm{Py}^{+} + \mathrm{Fe}^{2+} \tag{3}$$

$$\mathrm{Py} - \mathrm{Py}^{+}\mathrm{Py}^{+} \rightarrow \mathrm{Py} - \mathrm{Py} - \mathrm{Py}^{+} + 2\mathrm{H}^{+} \tag{4}$$

2. Bulk and suspension polymerization

A simple process in which the minimum of product contamination can be achieved in the polymerization of the pure monomer is called Bulk polymerization. In this polymerization, monomer suspends as droplets (discontinuous phase) (50–500 mm in diameter) in water (continuous phase) [1].

2.1 Ultrasound-assisted bulk polymerization of styrene

The results in the ultrasonic Bulk polymerization of styrene with AIBN as the initiator are listed and explained as follows:

1. Initiator concentration square root directly affects the rate of polymerization.
2. Enhancing net ultrasonic energy causes the total rate constant of polymerization to decrease linearly.
3. As sound energy is applied, an increase in average molecular weight is observed.
4. Ultrasonic waves affect the depression behavior of the gel.

The results also showed that the termination reaction rate rises and ultrasonic irradiation reduces the efficiency of the initiator [31].

2.2 Ultrasound-assisted bulk polymerization to fabrication of hydrogel macromolecules

Hydrogels are dense cross-linked polymers with three-dimensional network structures made from groups of functional hydrophilic which have significant water and solute molecules adsorbent ability. The swelling capability of the hydrogels is one of the key factors, considering the Polymerization methods, which is affected by functional units and the type of cross-linking agents, electric field, pH, ionic intensity, light, and temperature are the external affecting parameters that affect hydrogels [15].

Dispersions of monomer droplets and formation of free radicals were achieved by the assistance of ultrasound for initiation of polymerization of polymer hydrogel. Ultrasound irradiations create high shear gradients, which can control the molecular weights, and also through improvement in the adsorption ability of hydrogels and mechanical properties are able to enhance the particles dispersion in the polymer matrix [32].

Furthermore, initiation of bulk polymerization reactions to formation of polymer hydrogel by ultrasound-assisted synthesis from attachment of acrylamide and *N*-isopropyl acrylamide onto lignin by combination of montmorillonite with excellent swelling-deswelling property for the elimination of methylene blue from the aqueous medium is studied, and the results showed positive effects of ultrasonic on the polymerization process. Fig. 10 shows the schematic illustration of this process [32]. Also, in copolymers, the graft ratio, graft efficacy, and monomer conversion improved remarkably in ultrasound methods. Furthermore, the graft ratio and graft efficacy increased when one of the components and initiator were sonicated before the reaction prior to the addition of monomer [33].

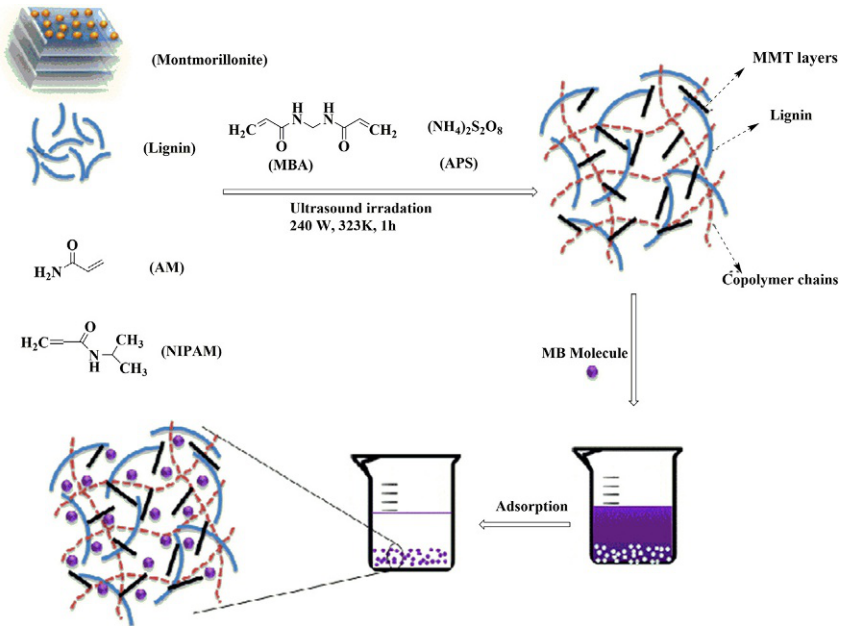


Fig. 10 Scheme for synthesis of hydrogel for the removal of methylene blue [32].

2.3 Ultrasound-assisted suspension polymerization of styrene

The suspension polymerization of styrene with the help of ultrasound is considered experimentally in a batch reactor and stirred continually. The following results are obtained from experiments:

1. Ultrasound prevents the agglomeration between droplets. Also, in batch and continuous reactors, it prevents the adhesive of droplets on the reactor wall during suspension polymerization.
2. The effect of the irradiation in the condition of 500 W at 400 kHz on the kinetics of suspension polymerization in batch operation was insignificantly unimportant, and so the rate equation of bulk polymerization under no irradiation represents the polymer yield and the average molecular weight of polymer.
3. The effects of the interactions between droplets in the reactor on monomer to polymer conversion and the average molecular weight in continuous operations by considering complete micro-mixing and complete segregation calculations were investigated. In micro-mixing, there are two stable steady states in a range of 6 where we can observe the gel effect, and also the droplet movements in the reactor will cause the interactions affecting the conversion and the average molecular weight of the polymer.
4. In the continuous operation, the results which occurred in between two very great conditions showed the considerable interaction between droplets [34].

2.4 Ultrasound-assisted suspension polymerization of 2-hydroxyethylmethacrylate/ethylene glycol dimethacrylate copolymer

As was illustrated before, the role of ultrasound in different kinds of polymerization is obvious Here we study the suspension Copolymerization of 2-hydroxyethylmethacrylate and ethylene glycol dimethacrylate using ultrasound (20 kHz). Different aspects of the process and the products such as shape, particle size, and development of the physical features (surface area, pore volume), which are affected by ultrasound, were observed continually and reported in the paper. Using ultrasound, they were able to prepare both smaller particles (10 μm) or larger ones (100 μm) since either way a narrower polydispersity PD) of sizes in the particles is possible [35].

3. Solution polymerization

In the solution polymerization process, the solvent acts as a diluent and supports the heat transfer process of polymerization reaction.

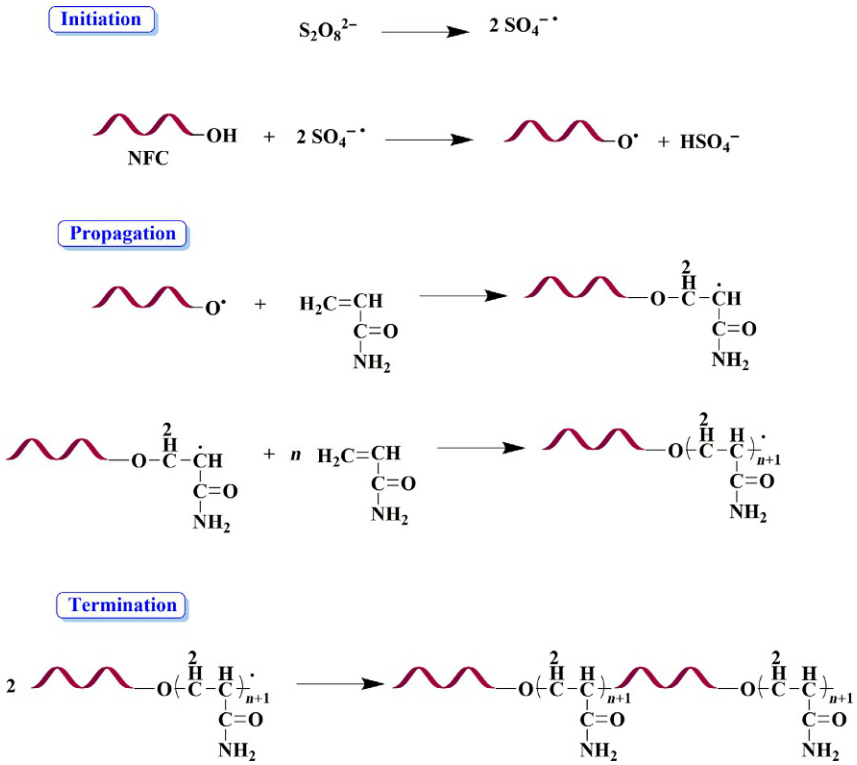
3.1 Ultrasound-assisted polymerization of acrylic hydrogels

In the preparation of acrylic hydrogels, ultrasound was employed to generate initiating radicals in the solutions of viscous aqueous monomer by glycerol, sorbitol, or glucose as potential additives in an open system at the temperature of 37°C [36].

Also, the cavitation effect of ultrasound in situ ultrasound-assisted polymerization of Polypropylene composite membrane with an acrylic hydrogel layer improves the attaching efficacy of acrylic acid on the membrane surface. It is necessary to mention that the ultrasound not only did not have a negative effect on the mechanical properties of modified membranes, but also there was a slight increase in mechanical characteristics of functionalized membranes owing to the presence of acrylic hydrogels, as was evident by the results of the experiment. This hydrogel can be a potential adsorbent for dyes and some salts in aqueous phases [37].

3.2 Ultrasound-assisted copolymerization of polyacrylamide/nano-fibrillated cellulose and acrylic acid/poly (vinylidene fluoride)

In the process of grafting the polyacrylamide onto nano-fibrillated cellulose (NFC-*g*-PAM) under ambient conditions, the ultrasound-assisted protocol had an intense influence in improving the attachment of PAM onto NFC (Scheme 1). Persulfate initiator and the ultrasound irradiation interactions causing the synergistic effect accelerate the creation of sulfate ion radicals as can be seen in Scheme 1. These radicals are responsible for the initiation and propagation of the polymerization practice [38]. In AA grafting onto PVDF, the grafting density of the reaction mixture could be controlled by changing the time and power of ultrasonic waves, monomer, and initiator concentration.



Scheme 1 Schematic representation for synthesis of NFC-*g*-PAM via an ultrasound-assisted method [38].

3.3 Ultrasound-assisted polymerization of poly (*N*-isopropylacrylamide-*co*-2-hydroxyethyl methacrylate)

Toward preparation of the copolymers with lower polydispersity index and with consideration to the polymerization rate and polydispersity of molecular weight, in the ultrasound-assisted polymerization of poly (*N*-isopropylacrylamide-*co*-2-hydroxyethyl methacrylate), without chemical initiator, the optimum volume fraction of ethanol was 60 vol%. The faster polymerization rate and lower molecular weight were achieved in advanced ultrasonic energy force, which was due to the higher number of radicals prepared in the reaction. In all the ultrasonic power intensities, the polydispersity was less than 1.5, so while maintaining low polydispersity, the molecular weight can be managed with ultrasonic energy force [39].

4. Phase-transfer catalysis polymerization

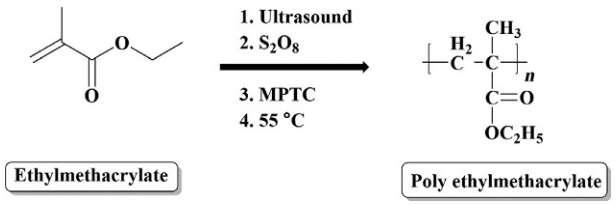
Phase-transfer catalysis (PTC) is important and such a convenient tool owing to its high conversion, simplicity, and high selectivity in different conditions and environments. Because of such properties, PTC can handle the interactions between immiscible lipophilic and hydrophilic reactants [40].

4.1 Ultrasound-assisted polymerization of butyl acrylate using crown ethers as PTC

The first study on this method was described by Rasmussen and Smith. They investigated the polymerization of butyl acrylate with several crown ethers as a PTC and initiators named potassium peroxydisulfate ($K_2S_2O_8$) which is soluble in water [41]. It was shown that the ultrasound improves the PTC efficiency with the production of high interfacial space through emulsification reaction that to enhance the interfacial contact area can create extremely fine emulsions. The reactivity of the reaction in a synergetic of PTC along with ultrasound is considered appropriate, which can result in some beneficial products [42].

4.2 Ultrasonic-assisted free radical polymerization of ethyl methacrylate using PTC

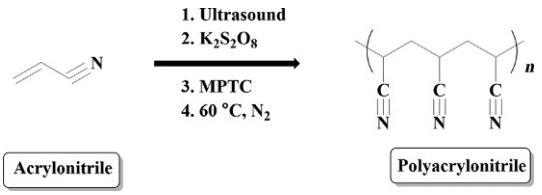
A novel dual-function, 1,4-dihexadecylpyrazine-1,4-diium dibromide was synthesized and was applied as PTC in the free radical polymerization of ethyl methacrylate assisted via ultrasound. The data of the experiment exhibited that the rate of polymerization enhances almost three to eightfold with 28 kHz (300 W) and 40 kHz (300 W), respectively, under ultrasonic medium (Scheme 2) [43].



Scheme 2 Reaction of polymerization of ethyl methacrylate [41].

4.3 Ultrasound-assisted radical polymerization of acrylonitrile using PTC

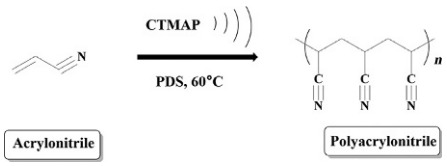
Selvaraj et al. reported the radical polymerization of acrylonitrile (AN) using ultrasound in a water/chlorobenzene biphasic system at 60°C assisted with multi-position phase-transfer catalysis. As mentioned above, the parameters involved in the polymerization rate revealed that the Rp enhances three to eightfold with 28 and 40 kHz underneath ultrasonic waves-assisted (Scheme 3) [44].



Scheme 3 Polymerization of acrylonitrile [44].

4.4 Ultrasound-assisted radical polymerization of acrylonitrile using PTC

Another study confirmed the importance of PTC and ultrasound combined techniques in active radical polymerization of acrylonitrile in two-phase conditions. The results of this study too showed the ultrasound effect on the rate of polymerization. The significant enhancement on the Rp was obvious by varying the experimental parameter under ultrasonic conditions. Ultrasound condition causes the fast dissociation of the initiator so that the production of more free radicals is possible and also the mixing of two phases can be improved. The polymerization of acrylonitrile (M) initiated using $K_2S_2O_8$/PTC in ethyl acetate/water is shown in Scheme 4. In the two-phase system, the PCT role (Q^+X^-) is to transfer the anion (Y^-) of the aqueous phase to the organic phase, at an area among the phases. Then, in situ reformed Q^+X^- in the aqueous phase is able to preserve the PTC polymerization practice as revealed in Fig. 11. Cavitations generated by the chemical effects of ultrasound are responsible for the generation of free radicals [45].



Scheme 4 Ultrasound-assisted phase-transfer catalyzed polymerization of acrylonitrile [45].

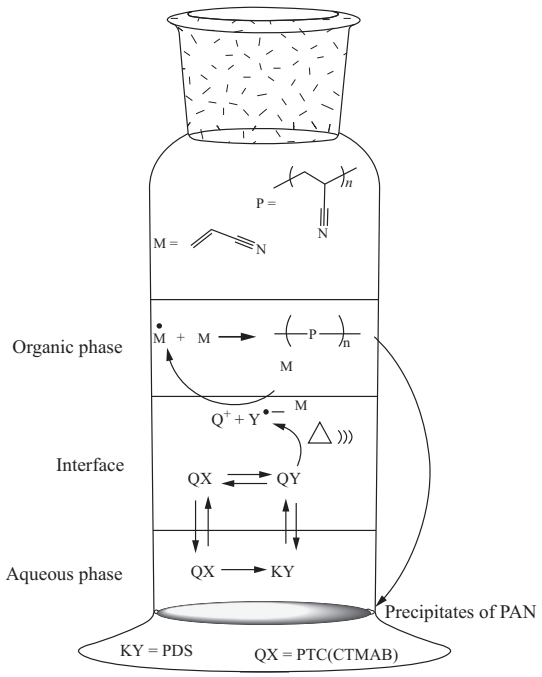


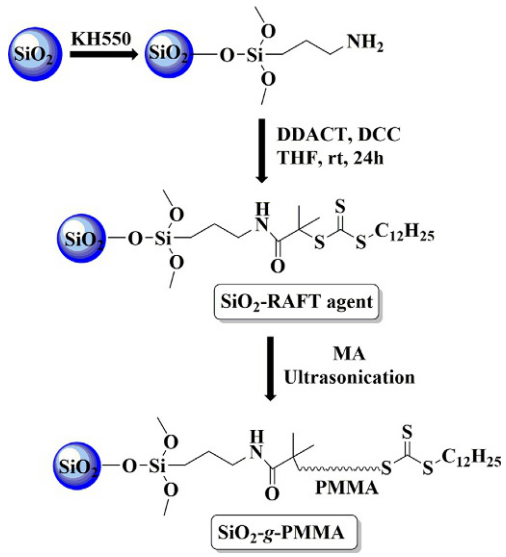
Fig. 11 Kinetic model of an ultrasound and PTC-assisted polymerization of acrylonitrile in a two-phase system [45].

5. Reversible addition-fragmentation chain transfer

Reversible addition-fragmentation chain transfer (RAFT) polymerization is defined as a living radical polymerization consisting of sets of reversible stages which work based on the degenerative chain transfer to convert suspended chains to an active propagating radical in a controlled reaction process [1].

5.1 Ultrasound-assisted graft modification of silica gel by RAFT polymerization

Silica gel graft modification with RAFT polymerization underneath ultrasonic waves has been investigated (Scheme 5) [46].



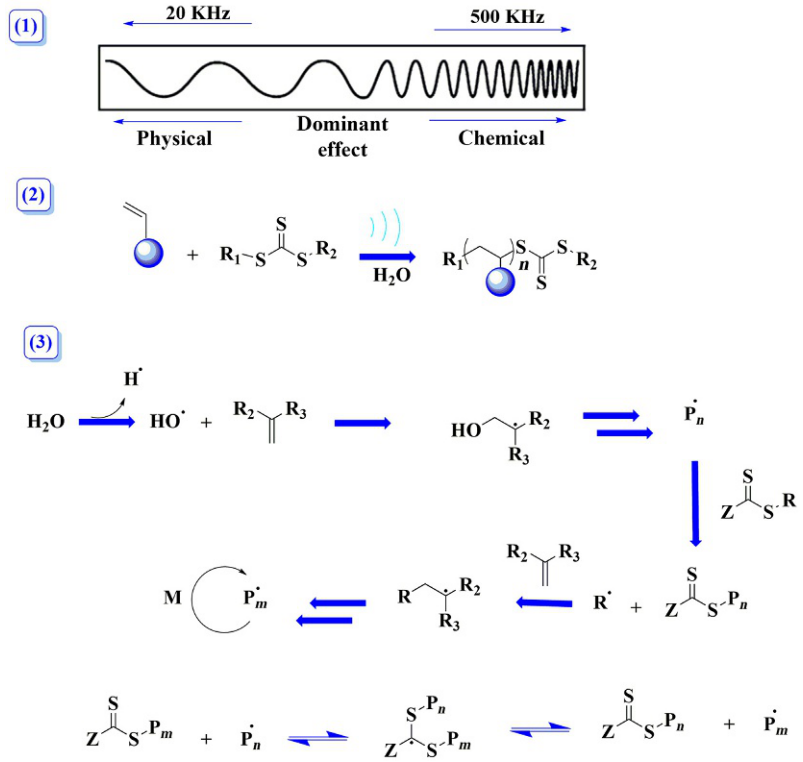
Scheme 5 The modification and graft polymerization of silica gel [46].

Ultrasound can be a proper source to initiate the radicals of a controlled radical polymerization when it occurs in the existence of a (RAFT) agent. This method is considered as a highly "green" approach of externally regulated/controlled polymerization which is able to directly point monomers or polymer structures in the process of polymerization. As was mentioned before, ultrasound causes the vaporization of liquid molecules into cavitation bubbles, which in fact will result in the formation of radical species, so that the growth of these species will eventually bring a collapse in the system. This anomaly is responsible for the generation of extreme localized pressures along with the areal heats, hence enabling the vaporization of so-called molecules into their related radicals.

Generally, there are two important effects of ultrasound needs to be mentioned:

- Physical strengths (i.e., high shear)
- Chemical effects (i.e., radical generation)

The frequency of the irradiation directly determines the extent of physical and chemical effects in a way that at low frequencies (~20 kHz) physical strengths are in the ascendant by the minimal chemical effects, while at higher frequencies (>200 kHz) we can observe the opposite behavior prior to the high frequency in the system (Scheme 6) [47].



Scheme 6 (1) Schematic representation of sonochemically induced RAFT polymerization (sonoRAFT); (2) proposed mechanism for sonochemical initiation of RAFT process; and (3) representation of forces generated under different ultrasonic frequencies [47].

5.2 Ultrasound-assisted RAFT polymerization-induced self-assembly (Sono-RAFT-PISA)

Reversible addition-fragmentation chain transfer by the polymerization-induced self-assembly process assisted with ultrasound (Sono-RAFT-PISA) is a "green" method in which the high-frequency (490 kHz) ultrasound is used. This reaction is done in the

existence of water as initiator and also as a solvent instead of organic initiator, namely *inisolv*, which can target the poly(*N*-isopropylacrylamide-*co*-*N,N'*-methylenebis (acrylamide)) P(NIPAM-*co*-MBA) as core and poly(poly(ethylene glycol) methyl ether acrylate) PPEGA as shell-based thermosensitive nanogels (Scheme 7).

Scheme 7 Synthesis of thermosensitive nanogels-based on PPEGA-*b*-P(NIPAM-*co*-MBA) [48].

Here some of the advantages of the Sono-RAFT-PISA approach are mentioned:

- Total monomer conversion
- Low temperature
- High polymerization rate
- Temporal control over the polymerization
- Usage of water as *inisolv*
- Lack of unused organic compound in the nanogels

The RAFT-PISA process, which is assisted with high-frequency ultrasounds, can acquire some benefits like:

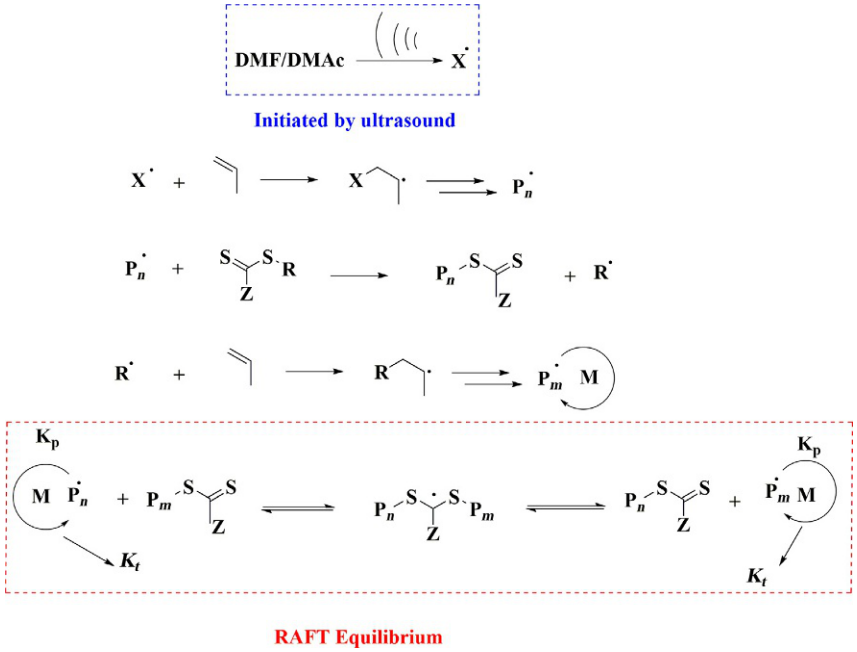
(1) Low reaction temperature
(2) Complete monomer conversion
(3) Lack of additional initiator

Schematic illustration of the RAFT-PISA process is presented as follows [48].

5.3 Ultrasound-assisted Sono-RAFT polymerization in organic solvents

Sono-RAFT in organic solvents such as DMF and DMAc with high-frequency ultrasonic power (490 kHz) showed that the polymerizations were commonly well managed by low dispersity of produced polymers. Monomer vapor pressure, solvent, and polymer nature influence the final monomer conversion and molecular weight association. In summary, the sono-RAFT process offers an ultrasound-assisted controlled polymer synthesis without the need for additives or common radical initiators [49].

The radicals (e.g., methyl radicals) which were produced via high-frequency (490 kHz)-stimulated pyrolysis of organic solvents ($X^{\bullet}$ in Scheme 8) can also initiate a polymerization. In this way, controlled sono-RAFT polymerization without the use of external additives or initiators in organic solvents is possible of being achieved (Scheme 8) [49].



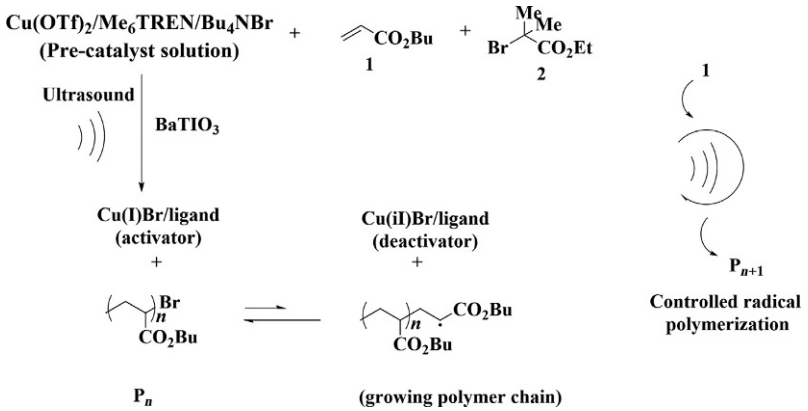
Scheme 8 Proposed mechanism of organic SonoRAFT [49].

6. Atom transfer radical polymerization

Atom transfer radical polymerization (ATRP) is referred to as a method in which the generation of a carbon-carbon bond by a transition metal catalyst is possible. The polymerization from this process is described as atom transfer radical addition polymerization (ATRAP) [1].

6.1 Ultrasound-assisted polymerization of acrylate by (ATRP) method

As an example, the polymerization of acrylate monomers provided by ultrasonic agitation is studied. Piezo-chemical reduction of Cu(II) in the attendance of a monomer of n-butyl acrylate and ethyl α-bromoisobutyrate used as the initiator will produce a low dispersity poly(*n*-butyl acrylate). Having a continuous increase of the polymer chain requires a continual ultrasonic activation of the chains during the process which is schematically presented as follows (Scheme 9) [50].



Scheme 9 Ultrasound-induced controlled radical polymerization of *n*-butyl acrylate 1. Sonochemical reduction of the Cu(II)/Me_6TREN complex at the interface of the piezoelectric nanoparticle ($BaTiO_3$) leads to the formation of the activator for ATRP. The polymeric chain growth starts from the alkyl halide initiator 2 and successive addition of 1 to the growing polymeric chain P_n occurs in a controlled fashion. The final polymer P_{n+1} is obtained after chain termination. P represents a polymeric chain with a degree of polymerization *n* [50].

6.2 Ultrasound-assisted polymerization of acrylate by (ATRP) method

Also, Methyl acrylate (mechanoATRP)[a] with low ppm of the $CuBr_2$/tris(2-pyridylmethyl)amine catalyst was carried out in an ultrasound chamber with narrow molecular weight distribution as can be seen in Fig. 12. [51].

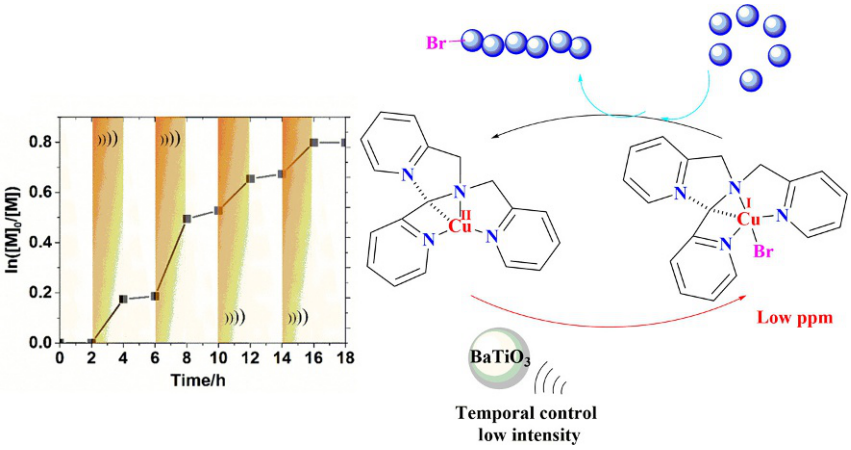


Fig. 12 Temporal control in mechanoATRP using $BaTiO_3$ nanoparticle (tetragonal, 200 nm) as a mechano-electric transducer under ultrasound agitation through intermittent switching on/off the ultrasound bath [51].

[a] Mechanically controlled atom transfer radical polymerization.

7. Ring-opening polymerization

Ring-opening polymerization (ROP) is another type of polymerization in which monomers such as amides, acetals esters, cyclic ethers, and siloxanes are used [1].

Ultrasonic of ring-opening polymerization in cyclic Bisphenol A polycarbonate oligomer can initiate the polymerization process and continually improves the reaction conditions; thus, no added chemical initiator is needed (Fig. 13.). Although having a chemical initiator in ultrasound-assisted polymerizations can significantly improve the polymerization rate compared to the initiator-free reactions, for example, if lithium salicylate is used as the initiator, the time of reaction would be reduced and the reaction would be conducted seven times faster than in initiator-free reactions [52].

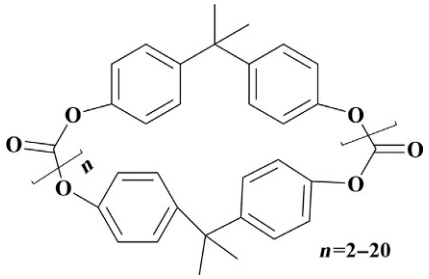


Fig. 13 Cyclic oligomeric bisphenol A polycarbonate [52].

In another research, ultrasound with higher intensities was used in δ-valerolactone and Ɛ-caprolactone ring-opening polymerization with dibutyl tin dilaurate used as a catalyzer in this reaction (Fig. 14). It was observed that the sonication creates better reaction conditions and accelerates the polymerization rate. In δ-valerolactone polymerization, using sonication can also improve depolymerization reactions which cause the molecular weight to drop during the reaction. The δ-valerolactone sequences caused the incorporation of Ɛ-caprolactone into the products which was the result of ultrasound usage in the reaction. This incorporation led to synthesizing copolymers from the so-called monomers [53].

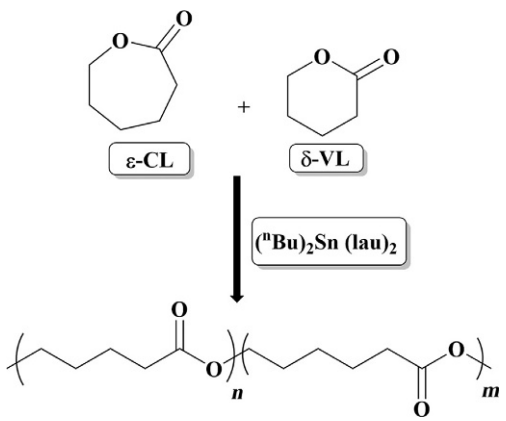


Fig. 14 Ring-opening polymerization of δ-valerolactone and Ɛ-caprolactone [53].

Gumel et al. reported the conversion of the gama-caprolactone to poly-6-hydroxyhexanoate and investigated the ring-opening polymerization process of this reaction. The initiation of the reaction is achieved through the lactone ring opening by the H_2O molecule in the complex media in which the molecule performs as a nucleophile on the intermediate complex of acyl carbon from acyl-enzyme in order to create hydroxyl carboxylic acid. The additional propagation of polymer causes the back side attack of the terminal hydroxyl unit on the complex which then results in the chain elongation process in which the monomer to polymer conversion occurs. This steps in this reaction are intensified in the presence of ultrasound that affects the catalytic behavior, chain propagation steps rate, and the process of monomer synthesis, and thus the polymerization rate is improved. Enhanced micro-streaming confirmed by the results of characterization, revealed that the sonication synthesizes a polymer with excellent crystalline structure compared to the sonication-free process in which the crystallinity is 61% and 21%, respectively. This micro-streaming provides an alignment of polymer molecules in the presence of ultrasonic irradiation. As results after 90 hrs, the poly-6-hydroxy hexanoate polymer molecular weight was much higher (twice) in sonicated conditions than non-sonicated ones [54].

8. Conclusion

The chapter mainly focused on characterizing the different aspects of the energy resulting from ultrasonic which mostly causes the degradation of polymer chains in a case where the produced radicals are the keys for the polymerization process to be started. The discussion here included some ultrasound-assisted polymerization processes such as Emulsion Polymerization, Bulk and Suspension Polymerization, Ring-Opening Polymerization, etc. To conclude, ultrasonic waves are one of the most used approaches for the dispersion of monomer into the medium of complex solutions where there is no need for excess or any chemical initiator. The results reveal that the process of ultrasonic-assisted polymerization is easily controlled by the properties provided by means of ultrasonic waves in which case there is no need for chemical stabilizers. Also, according to the kinetic studies mentioned in the chapter, the polymerization rate, decrease in polymer size, and molecular weight distribution are directly influenced by the properties of the ultrasonic energy so that the consideration of different outcomes of the reaction products can be manipulated along with the engineering of the ultrasonic energy to form a condition which will result in a most efficient product.

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CHAPTER 13

Sonochemical methods and their leading properties for chemical synthesis

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1. Introduction

Rarefactions and alternate compressions in a transmitting medium with wave having a preparation direction form an acoustic wave called ultrasound. Ultrasound or acoustic waves have been accepted as a vital process for the synthesis of organic and other chemical syntheses. A liquid is subjected to external ultrasonic pressure; the weak bonds between the molecules firstly began to be weakened. Van der Waals, the weakest of physical interactions, tears first. In addition to this weakening of the physical bonds, microbubbles formed by gases and, as a result, chokes occur. The rapid movement of micro-sized microbubbles forms from the nucleation and collapse-growth of these nuclei and formation of cavitation patterns [1,2]. The sonochemical effects of cavitation patterns result in the formation of high energy waveforms. Sonochemical effects enable the formation of high energy particles and their distribution in the solution medium. Sonochemical effects facilitate the interaction between a substance and catalyst that enhances the activation of the metal surface. These effects cause the formation of high temperature (4000–5000) and high pressure (close to 1000 atm) in a short time [3]. As can be understood, the ultrasound cavitation waves facilitate events such as reactive diffusion from the solution medium to metal, electron transfer, and reduction of organic substrates on the active surface. Hence, new metallic organic frameworks are formed by the acoustic wave and cavitation effects under ultrasonic conditions [4].

2. Ultrasound operation and bubble formation

Ultrasound operates at a frequency in the range of 10–20 kHz and acts as an acoustic mechanical wave. With secondary and cavitation effects, ultrasound gives high energy the medium in which reaction takes place. In the ultrasound process, various microbubbles inside the solvent vapor are formed, and that produces acoustic energy with radial

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motion through the reaction medium. The size of microbubbles reaches a stable and transient diameter in the range of 4–300 μm [5,6]. The microbubbles having a low acoustic intensity and numerous acoustic cycles repetitively and periodically enhance and shrink. A few microbubbles of sufficient acoustic energy density may remain unstable within the acoustic cycle formed. When the resonance frequency of the microbubbles reaches a level that exceeds the ultrasonic field value, the bubbles formed collapse, having some unique physical-chemical effects trigger the biochemical or thermochemical reactions. The formation of microjets with high velocity occurs because of some unsymmetrical movements of bubbles to the surface solid or inside of a solvent. These unstable movements of bubbles occur as collapse of the bubbles that lead to the formation of a strong shock wave, which may reach up to 103 MPa [7]. The movement of liquid toward the cavitation parts caused by ultrasonic waves allows the concentration of solid and fluid movement. These concentrated solid and fluid movements cause the formation of emulsion or miscarriage. Compared to conventional methods, in the ultrasonic process, some sharper forces are formed, and these forces divide liquids into small droplets and divide solids into finer particles. The ultrasound causes two types of formation of bubbles, which are a single bubble and multi-bubble systems. In a single bubble, one process is conducted, but two processes are performed in the multiple systems. The mentioned processes conducted in these systems are called bubble coalescence and rectified diffusion. In the single system, the influencing growth of bubbles is investigated using some different experimental methods containing stroboscopic, light scattering, and video recording. The abovementioned experimental procedures cannot be applied to multiple methods [8]. The bubble growing processes contain various complexities; for this reason, some researcher [6] developed a facile method about the bubble growing in the multiple systems that allow to record the bubble coalescence and diffusion qualitatively. In order to get a steady state of multi-bubble formation in the aquatic medium, so many acoustic pulses must be generated under sonication conditions or the high frequency of ultrasonic values. The nonpresence of bubbles with a resonance size at the beginning of the sonication process is effective on this steady-state formation of bubbles [6].

3. Effectiveness and parameters of the sonochemical process

To determine acoustic cavitations, processes, and raw materials, various experimental parameters including design of devices, ultrasonic frequency, homogeneity of solvents, temperature, the pressure of the fluid, and state of power dissipation in liquid are conducted. To specify the systems for ultrasonic studies, power values of acoustic levels are presented in various contents for instruments. The reactors as specific instruments containing rating values may be viewed for use in specific sonochemical processes, although

the rating values viewed on the reactor are not real values in the process because of energy losses during the energy conversion or transformation. The real energy level during the process in the reactors is varied, almost about 10%–40% values [5]. The amounts of power and energy values are largely expressed by the volume or scale of the process. However, calorimetric measurement is also used in determining the power level. The volume of liquid in probe-type reactors is expressed as the actual volume of the reagent. The water in the bath in the reactor used for the sonication process serves as the first receiving medium in the event of ultrasonic irradiation. The factors affecting the sonication process and the amount of energy emitted are factors such as bubble life, bubble chemical composition, bubble settling time, and variation in size shape in the bubble radial motion structure. High cavitation and acoustic density values with low thresholds may be effective in obtaining multiple bubbles [9]. However, the effect of different factors on the difference in the densification processes may be different. In the event of bubble collapse, the energy release rate and intensity are effective on the waves generated by the shock wave and micro-convection condensation. For this reason, the bubble length elongation-shortening, bubble chemical content, bubble collapse time, and heat capacity must be formed at the density level formed. For an effective sonication function, it is important to shorten the sonication timing and to ensure that radicals accumulating in the blister are removed. In addition, volatile substrates in the blisters need to be provided during chemical densification. Heterogeneous systems designed for nonvolatile liquids or fluid viscosity are other factors that affect energy absorption. The optimization of these bet parameters should be performed precisely in the case of real condensation functions and the realization of specific reactions [9].

4. Intensives and frequencies of sonochemical irritations

Ultrasonic frequency is a significant issue because it affects the features of bubble cavitation in forming the acoustic cycle during the process of operating at high and low frequencies. As mentioned above, information determining an appropriate frequency of irrigation is a very important issue in sonochemical devices for chemical processes. The studies about the sonochemical process revealed that an effective physical process requires sonochemical irradiation having at least about 10–100 kHz [10]. The irradiation with this frequency range is applied for the conversion of biomass into biofuels containing biodiesel synthesis, extraction, polymer degradation, bioethanol, etc. The irradiation having a frequency above these values can be applied for chemical synthesis needed for intensive conditions for some conversion processes and synthesis studies containing water or aquatic mediums [11,12]. Some researchers [13–15] investigated potassium iodide oxidation reaction under sonochemical conditions using various sonochemical devices to determine the effects of frequent irradiation difference.

A maximum rate for oxidation has been detected in a potassium iodide decomposition process conducted with some different frequency in the range of 20–500 kHz. In another study [16], it was determined that a high frequency induced a reverse influence because of insufficient energy distribution (19.5 kHz–1.2 MHz). Some similar results have been detected in other studies that addressed fixing a high 130 kHz efficiency in the Fricke mixture under sonochemical conditions. The optimum frequency values for sonochemical research have been studied and detected by previous searches [16]. The notion of enough time at high frequency led to a decrease in acoustic energy at the sonochemical condition. After all, the high-frequency level at ultrasonic conditions results in positive situations on energy efficiency and power distributions. In some paper, it has been reported that the high-frequency level induces an acceleration in free radical reactions [17]. Additionally, the ultrasonic cycle duration is shortened at high frequencies that accompany with enhancing useful cavitation during the short time of the process, and the presence of free radicals may influence the expiration of bubbles. In the literature, studies conducted at different frequency values (20–1056 kHz) revealed that formation of the volume variation of bubbles at low frequency was higher than that in the high-frequency medium that shows a low energy liberation at a lower temperature [18]. An acoustic cycle forming occurs by water evaporation. The extension of the duration and the growth of bubble size of cavitation bubbles at low-frequency values cause the entry of more liquid molecules inside the bubbles having high energy. However, the cavitation efficiency and released energy rate of single bubbles have been higher than bubbles originated at high frequencies by some researchers [19].

5. Duration of stirring

Durations for stirring mixtures are very effective factors in a process conducted in sonochemical instruments and are extensively studied to detect its effects on sonochemical operations and parameters. Effects during chemical reactions of sonochemical reactions are getting more evidence as the reaction progresses. Mixture stirring duration and reaction time are important factors to get a completed process for synthesis or the other reaction studied. A reaction occurring with a high reaction rate take places randomly. For this reason, the stirring mixture must be shorter than the reaction time to get a completed reaction in sonochemical instruments [20–22]. Hitherto, various methods have been used in the conventional instruments for the measurements of mixing durations. Some of these methods including conductivity, fluid dynamics, pH, and particle size-image are also applied in the sonochemical process and sonochemical instruments for different chemical applications. In these studies, variations of power, energy, and ultrasonic frequency are investigated depending upon stirring mixture time in sonochemical instruments. Studies conducted for the identification of models of various chemical

reactions in batch or semi-batch sonochemical instruments have been tested and should be tested for further research. Hitherto, searches related to sonochemicals revealed that increase of ultrasonic intensity decreases the stirring time. Additionally, the increase in the amount of ultrasonic intensity generated from power has a reducing effect on mixing time [23].

6. Heterogeneous and homogenous features of reactions under ultrasonic conditions

Active cavitations in reactions-based ultrasound assistance under sonochemical conditions take place on the heterogeneous sides of liquids. The heterogeneous sites in liquids used for sonochemical studies are nuclei formed from collapse, free microbubbles, additives of nonvolatile, impurities fragmentations, etc. The spectrum for water containing any impurities and pure water shows no production of fundamental frequencies for an ultrasound with only one peak. On the other hand, water containing a certain amount of gas microbubbles produces an acoustic emission with harmonic, ultra-harmonic, and strong subharmonic emission spectrums. For these reasons, the heterogeneity of reactions studied is a requirement for producing ultrasonic cavitations [24,25].

It can be understood that chemical and physical features of liquids as solvents affect the formation of acoustic cavitation and propagation. Chemical features of liquids containing electrolyte activity, radical content, and the composition of ternary-binary organic mixtures influence the physical properties like volatility, viscosity, and the surface tension of multicomponent-single liquids. These properties of liquids have a vital effect on the activity of sonochemical reactions [9]. The interaction of intermolecular is a breakdown and weakens upon the formation of cavities in a bulk solvent structure under ultrasounds. The variations in the interaction of intermolecular determine the physical properties like vapor pressure, surface tension, viscosity, and boiling point of liquid under ultrasonic conditions. A liquid having a high vapor pressure, surface tension, viscosity, or boiling point prevents energy enhancement, which produces cavities for bubbles. The chemical contents and physical properties of bubbles are influenced by oscillations of the growing size of the surface tensions, the volatility of liquid, and cavitation bubbles. High volatility prevents the collapse of bubbles and induces a form of intensified bubbles. The high surface tension of liquid ensures a stable bubble size that prevents the dissolving of bubbles into a bulk solvent [9]. Ultrasonic or hydrodynamic cavitation enables an effective effect by catalyzing with low energy under room conditions. Hydrodynamic cavitation is a facile and effective method, especially in some common applications such as oil hydrolysis, oxidation process, depolymerizations, removal or degradation of pollutants, and organic syntheses. By using hydrochemical cavitation, distinguishing real chemical effects from mechanical effects is possible, and this method enables some unique advantages of pressure waves in the synthesis materials in modern chemistry. The applications and processes

of ultrasound have not been highlighted well as yet. However, its importance and effectiveness in synthesis materials have been captured by industrial and academic fields [1], because cavitation effects occurring from ultrasounds have some huge and useful effects on the accelerating chemical conversion reactions of heterogeneous systems and processes. Enabling shorted the reaction time, while inducing selectivities and enhancing reaction yields are some distinct and effective features of cavitation of sonochemical in experimental processes. Methods containing metal catalysis and called synthetic techniques have been extensively applied and seen as a rewarding issue and favorite in sonochemical processes [26–35]. Generally, the studies conducted in sonochemical syntheses are carried out in an aqueous or water medium for heterogeneous reactions. The aqueous or water medium enables a sufficient medium for producing excellent cavitations from mild conditions up to 60°C [36]. As is known, water is naturally being abundant, environmentally friendly, nontoxic so that it can be a good dispersible medium for producing cavitations under the mentioned conditions. Compared to nonaqueous environments, the sonochemical events in water highlight the visibility of chemicals with reactive and selective effects. As a result of the studies on the subject in the literature, the best solvent to be used is a solvent-free process. However, the best answer to this question is water [36].

7. Conversion of biomass to biofuels under ultrasonic conditions

In addition to the chemical synthesis processes, the sonochemical method has a wide application area in the conversion of biomass to biofuels. Sonochemical processes in biofuel and related fields are numerous. These processes include pretreatment of lignocellulosic structures, sonochemistry of carbohydrates, natural product extraction, fermentation, organic waste pretreatment, biological water treatment, and biotechnology/bioengineering [37–39]. In these mentioned applications with ultrasonic support, the future advantages of the ultrasonic reaction mechanism, ultrasonic condensation, and ultrasonic pretreatment applications need to be evaluated very well. In the studies examined to date, the effects of lignocellulosic structures, microwaves, and biodiesel on sonochemical pretreatment applications and biomass conversion rates have been studied and explained. The conversion of biomass into biofuel contains some difficulties to be overcome. In order to overcome these difficulties, the structures in the structure of the biomass should be illuminated. Raw biomass contains various structures containing lignin, cellulose, hemicellulose, free sugar, beeswax, proteins, trace organic-inorganic, and alkaloids, such as a large number of complex structures. Almost the whole of these structures in biomass are indefinite chemical structures. Cellulosic structures in biomass have a continuous repetitive structure, and lignin complex has a reticular connection structure [9]. The degradation of the lignin-carbohydrate structure in the raw biomass requires a high temperature-pressure environment, namely, harsh conditions. The selection of the appropriate solvent for the

degradation of the structures in this biomass is one of the issues that should be considered carefully in biomass conversion. Ultrasonic energy can be an appropriate tool for overcoming these troublesome problems, because it provides suitable physicochemical conditions in the processing of complex structures in biomass. Compared to thermochemical methods with the introduction of high-intensity ultrasonic energy into the biomass, the conversion of biomass under lower valence conditions leads to degradation and high-efficiency catalytic reactions. With the applied ultrasonic energy, heat and mass transfer in the reactions take place at high intensity. The intermediate causes the contact of reagents and products to increase, and the reaction kinetics accelerate [9].

8. Features of sonochemical reactors and devices used for sonochemical synthesis

There are several types of ultrasonic devices used in the laboratory for sonochemical studies. The devices used in laboratory-scale studies include biodiesel transesterification, microfiltration, ultrasonic horn, sacrification, and micronization tools [40–43]. Energy consumption level, durability, efficiency, usability, and flexibility are among the features that are required in the devices to be used for sonochemical synthesis *reactions*. In the ultrasonic devices, there is a horn in the liquid which provides the formation of the wave and a probe which enables the propagation/transmission of the formed wave to the environment. The probe is mostly made of titanium and has a diameter of 5 mm–1.5 cm. The wave generated by the horn is of high intensity near the probe. This high-density branch can be used effectively in processes requiring high mixing [44–46]. In order to process the biomass using ultrasonic methods, adjustments such as appropriate power, frequency, and temperature of the devices to be used should be made. In addition, it should be noted that the solvent to be used, the processing time, and the device with the appropriate geometric structure are also so important. The adequate size and proper structure of the device to be used affects the energy level and distribution to be spent. Thus, it is necessary to achieve the desired effect without disturbing the structure of the material to be worked on. As can be understood, the adjustment of these data will affect the efficiency and reliability of the results. Of course, the experimental optimization and preliminary procedures will be different from study to study. However, appropriate parameter selection and other common effects such as reactor, wave density, oscillation-emission, wave life, radial oscillation, micro convection, and shock waves should be applied by the literature. Probe type reactors and baths are widely used in laboratory studies due to their inhomogeneous distribution, i.e., heterogeneous acoustic effect and low energy distribution. Fig. 1 shows an ultrasonic horn reactor with an operating frequency of 20 kHz. Fig. 2 shows a common horn reactor used for sonochemical studies in laboratories, and the operating frequency is 36 kHz [47].

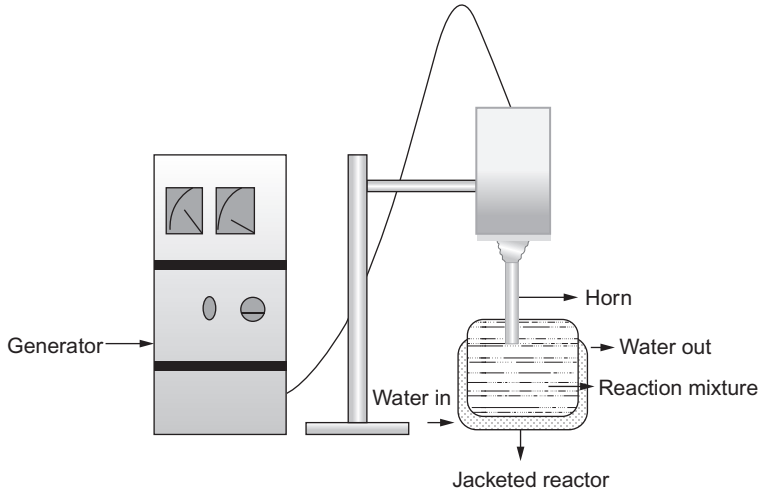

Fig. 1 Ultrasonic horn reactor (20 kHz) [47].

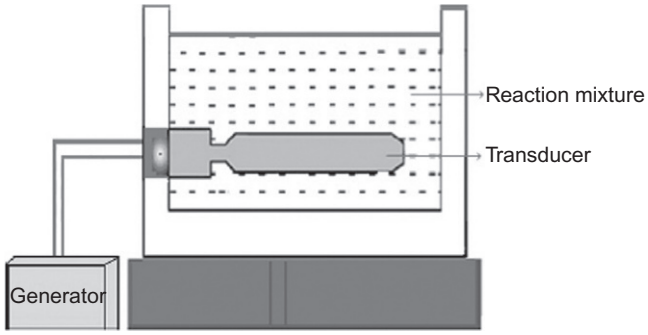

Fig. 2 Ultrasonic longitudinal horn reactor (36 kHz) [47].

9. Conclusions

In the ultrasound process, various microbubbles inside of solvent vapor are formed, and that produces acoustic energy with radial motion through the reaction medium. The size of microbubbles reaches a stable and transient diameter in the range of 4–300 μm. The microbubbles having a low acoustic intensity and numerous acoustic cycles repetitively and periodically enhance and shrink. A few microbubbles of sufficient acoustic energy density may remain unstable within the acoustic cycle formed. When the resonance frequency of the microbubbles reaches a level that exceeds the ultrasonic field value, the bubbles formed collapse, having some unique physical-chemical effects triggering the biochemical or thermochemical reactions. High cavitation and acoustic density values with low thresholds may be effective in obtaining multiple bubbles. However, the effect

of different factors on the difference in the densification processes may be different. In the event of bubble collapse, the energy release rate and intensity are effective on the waves generated by the shock wave and micro-convection condensation. For this reason, the bubble length elongation-shortening, bubble chemical content, bubble collapse time, and heat capacity must be formed at the density level formed. The degradation of the lignin-carbohydrate structure in the raw biomass requires a high temperature-pressure environment, namely, harsh conditions. The selection of the appropriate solvent for the degradation of the structures in this biomass is one of the issues that should be considered carefully in biomass conversion. Ultrasonic energy can be an appropriate tool for overcoming these troublesome problems. Having sufficient knowledge about the features and characteristics of sonochemical reactors leads to appropriate design and obtainment of optimum operating parameters which plays a crucial role in process efficiency based on specific applications. Energy consumption level, durability, efficiency, usability, and flexibility are among the features that are required in the devices to be used for sonochemical synthesis reactions. Choosing the suitable type of transducer with the proper frequency range and power intensity, several transducers and their positions in the reactor can be extremely effective in optimizing the cavitation activity, acoustic streaming, and enhancement of sonochemical reactor efficiency. In the ultrasonic devices, there is a horn in the liquid which provides the formation of the wave and a probe which enables the propagation/transmission of the formed wave to the environment.

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GREEN SUSTAINABLE PROCESS FOR CHEMICAL AND ENVIRONMENTAL ENGINEERING AND SCIENCE

Sonochemical Organic Synthesis

Covers developments and potential applications of ultrasound in a sustainable and environmentally friendly chemical synthesis in the organic and pharmaceutical chemistry.

Edited by
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Green Sustainable Process for Chemical and Environmental Engineering and Science: Sonochemical Organic Synthesis focuses on synthesis purification and extraction of organic, biological, and medicinal compounds using sonochemistry. It provides readers with an understanding of green ultrasound-assisted chemical synthesis for industrial applications. This book systematically explores the application of ultrasound in organic synthesis of all types and includes stereoselectivity, regioselectivity, oxidations, reductions, protection, deprotection, additions, condensation, coupling, C-X bond formation, named reactions, heterocyclics, biological drugs, and fluoroorganics over conventional techniques. A brief introduction to the parameters which influence the process, solvent-effects, supported reagents and catalysis and the pros and cons to the practical use of sonochemical protocols in organic synthesis are also discussed.

This book provides overview on the applications of sonochemical technology for the sustainable and environmentally friendly development of synthetic methodologies for organic and pharmaceutical chemistry. Sonochemical Organic Synthesis is an essential resource on green chemistry technologies for academic researchers, R&D professionals, and students working in modern organic chemistry and medicinal chemistry.

- Offers a broad overview of ultrasonics-assisted green organic synthesis
- Discusses sonochemical technology for green organic synthesis and also biological medicinal importance
- Gives details account of the numerous industrial applications such as polymers, pharmaceutical, fluoroorganics, biofuel, carbon, etc.
- Includes a description of the significant factors and challenges of the ultrasonics-assisted green organic synthesis
- Lists recent developments in the use of sonochemical technology in organic chemistry

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The book provides an all-round knowledge in computer fundaments in details , C and object oriented its completion while clearing the basics in computer hardware and software. The essential concepts of C and object oriented concept are supported by well-annotated and properly indented programs. Every program in this book has been adequately explained. Many of these programs are based on real-life situations that readers can often identify with. Wherever possible, a program has been progressively enhanced with the exposition of a new feature of the language.The author has used simple language for critical explanation supported by strong pedagogical features. The book is logically organized. The chapters are incorporated with illustrative examples to add analytical insight on the subject.

Dr. Marpe Sora obtained B.Tech form NERIST, M.Tech from Tezpur University and PhD, Guwahati University. Presently he is Sr. Assistant Professor in Rajiv Gandhi University, Department of Computer Science and Engineering Arunachal Pradesh. His main research interests include Signal and Speech Processing and Data Mining.

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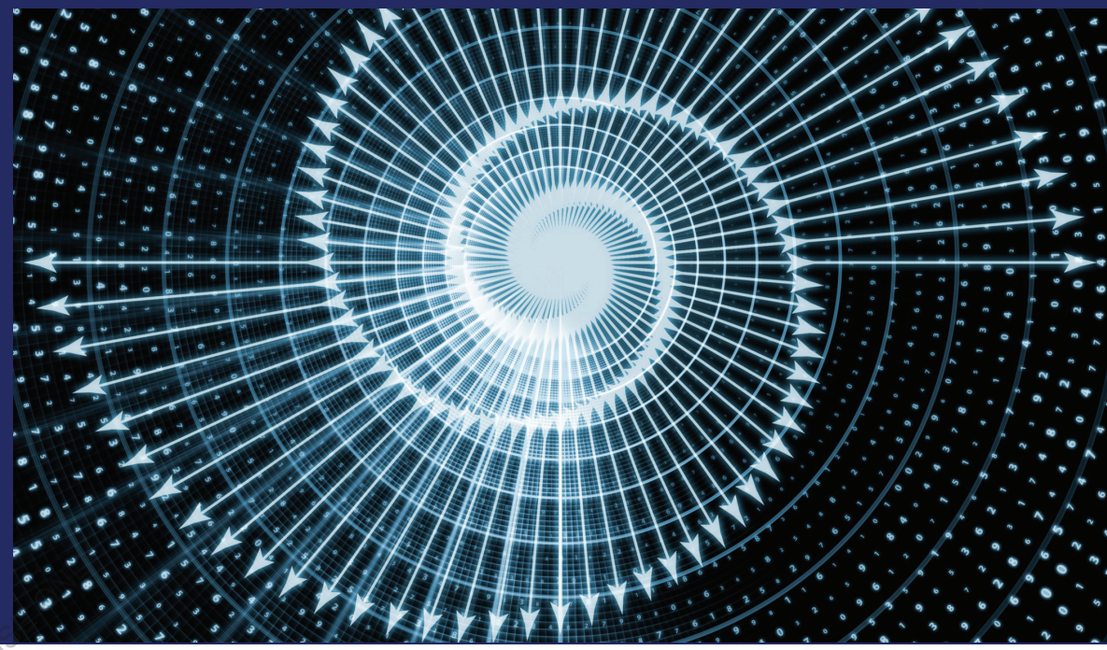

Marpe Sora

Computer System and Programming fundamentals in C

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CHAPTER 1

INTRODUCTION TO COMPUTERS

1.1 What is a Computer?

The hallmark of computers is their "computing power" which enables them to perform calculations, comparisions and manipulation of data with high speed, accuracy and reliability. A computer is an electronic machine which performs complex arithematic and logical operations on large volumes of data using pre-defined instructions written by human beings with high speed and accuracy and produces the desired output. Computer programs may be written in high level languages like C, C++, Java and so on. Some programmers also write assembly language to carry out the desired task. In a nutshell, a computer is fast accurate and reliable machine that accepts and store input data, process data produces output result under the direction of a stored program of instructions.The letters of the term "COMPUTER" may be interpreted as C=Calculate, O=Operate, M=Manipulate,P=Print,U=Update,T=Tabulate, E=Edit and R=Response.

Computers can store a vast amount of information and retrieve it at extraordinary speeds. They do not forget anything, and straightaway get on to the job without complaining. All the organizations have became so much dependent on the computers that without computers society would no longer function.

1.2 Data and Information

Data, are collection of numbers, letters of alphabets or some facts comprising of figures and numbers. Data on their own are not that of useful unless they are arranged or combined with some more useful data. For instance, Mr. Peken scored 97 marks out of 100 in a mathamatics test.

Information is meaningful/systematic organization of data. Information on its own is useful, but data may not be. Normally, information is obtained from data only after processing.

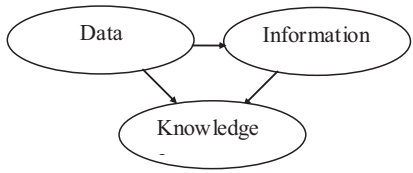


Figure.1.1 Data processing cycle.

The work that is done on data is called data processing. This processing could be anything like multiplication, addition, subtraction, division or comparison. The computer processes raw data to obtain information. This information is used to acquire knowledge. This knowledge in turn can be used as data for future use.This data processing cycle is illustrated in above figure 1.1.

1.3 WHAT DO COMPUTERS DO FOR US?

Computers provide means to us for disseminating information by collecting, storing, encoding, processing, analyzing, transmitting and receiving, printing text, audio or video. In fact the computer, it regulates all the aspects of our lives including how we live, how we work, how we communicate, how we relax, how we travel and how we walk. Hence, the computer is an instrument for four future progress.It has became an integral part of our professional lives. The evolution of computer is being more and more directed towards the benefits of society. Some such examples are given below:

1. The computer has made the world incredibly smaller by facilitating communications.
2. The computer has help advanced science and medical discoveries more in the last 10 years than in preceding centuries of history.
3. The computer has helped design cars, roads, cities, clothing, etc.
4. The computer has exploded our imaginations with colour and virtual reality.
5. The computer has opened freedom of speech to areas all over the world via the Internet.

…. The list goes on and on. The computer has magnificently performed to shape the modern world some good and some bad. In all, it has been a great blessing when properly used.

1.4 EVOLUTION HISTORY OF COMPUTERS:

Computers have wedged themselves into every facet of our lives.In order to properly understand and appreciate the progress made by mankind and to anticipate the continued evolution of society, let us look at the history of progress of the computer. Computers have been around for almost 150 years (Brigham Young invented a device to calculate the number of miles a wagon traveled by counting the number of wheel rotations). There have been all types of machines built to compute or measure various things (there is even one that will compute a logarithm). Most of these machines have been “analog” or value-based. Analog machines can represent any value between zero and one, or for that matter any value between two adjacent integers,just as any numer between zero and, say a million. An example of an analog device is the odometer in a car. There was another type of early machine which used a magnet-powered switch would close when the electromagnet was turned on (this kind of switch is the switch a “relay”).The advantage of using switches (either “on” or “off”— called “digital”) was that the results would always be predictable (the value will always be a zero or a one). On the other hand, analog devices always have to be tuned (just try to put a different sized tyre on your car). The problem with relays is the power required and the delay experienced in switching was too great to make them into a computational device. Early computers, therefore went a different route by adopting electron (or vacuum) tubes, instead of the on-off relays.

The invention of a mechanical adding machine in 1642. ABACUS, an early computing tool, the invention of logarithm by John Napier and the invention of slide rules by William Oughtred were significant events in the evolution of computers from these early computing devices. Around this period only, Herman Hollerith came up with the concept of punched cards, which were extensively used as input media in computers in late 1970s. Some of well-known ancestors of modern computers are as follows.

1. The earliest device that quantifies as digital computer is the “Abacus” also known as “Soroban”. This device permits the users to represent numbers by the position of beads on rack.
2. Pingala introduced the binary number system, which would later form the core of computing systems.
3. Later in 60 AD, Heron of Alexandria invented machines that could follow instructions.
4. The 1600s witnessed the invention of slide rules, the system of movable rods based on logarithms used to perform basic mathematical calculations, and a mechanical adding machine, which in some way, laid the foundation of modern-day calculating machines or computers.
5. Charles Babbage designed the first mechanical computer in 1822 and the Analytical Engine in 1834. The Analytical Engine contained an Arithmetic Logic Unit (ALU), basic flow control, and integrated memory and is the first general-purpose computer concept.

In the mid 1950s, a special little switch was invented that has since then reshaped our history the transistor, a little thing less than one inch compared to 3-4 inches height of a vacuum tube and its power (much less than a watt— compared to 5-10 watts).

Modern computers are composed of millions and millions of these transistors switches, arranged in arrays to accomplish what we ask of them. Your computer memory alone has millions of transistors—one megabyte has one million bytes or eight million bits. That’s more than 8,000,000 transistors!

Personal computers have been around as early as the mid-1970s. The early companies involved included Apple, Commodore, Atari, Synclair, to name a few. The early chips for these computers only had 10-50 thousand transistors. At that time personal computers were not taken seriously and were infrequently used in the workplace.

The first attempt to make a business-directed personal computer was by Apple when they introduced the Lisa computer. That was a failure mostly due to $7000 price tag. The next was the Macintosh which was better received. The growth of personal computers did not really take off until the IBM entered the market. From their open architecture, hundreds and thousands of computer companies sprang up. All the while technology advanced at a tremendous rate. Also, due to advances in chip manufacturing, the prices plummeted.

1.5 GENERATIONS OF COMPUTERS EVOLUTION:

Computer evolution is categorized into five generations based on the period of evolution and the technology used as listed in the following table.

Table 1.1 Technology used in different Generations in Computers

Generation	Hardware	Operating Systems	Year of Introduction	Examples	Charactersics
First	Vacuum Tube	None	1945	The Mark1 Computer	Punched card machinery, complex in design and huge size
Second	Transistor	None	1956	IBM 1401	High speed card punching and reading, magnetic tape input and output, high speed printing, stored program, and arithmetic and logical ability.
Third	IC Techlology (SSI, MSI)	Yes	1964	UNIVAC 1100, IBM 370	It was used for business and scientific applications
Fourth	IC Techlology (LSI, VLSI)	Yes	1971	VAX 11/780	Large systems with more processor
Fifth	HAL	Yes	1989	SPARC	High-performance microprocessor

1.6 TYPES OF COMPUTERS:

Based on the physical size, complexity of tasks performed etc. computers can be categorized into different types as listed in the following table 1.2.

Table 1.2 Types of Computers

Computer Type	Year of Introduction	Examples
Mainframe	1945	Mark1, IBM 370, UNIVAC 1100
Minicomputer	1965	PDP 8, PDP 11
Microcomputer	1972	WIPRO 86, SUPERMAX
Personal Computer	1975	APPLE PC ,IBM PC
Laptop	1983	IBM 5155, Compaq 286
Palmtop	1990	HP 95LX

1.7 MICROPROCESSOR EVOLUTION:

The microprocessor, from the onset of personal computers, has been the driving force of hardware and software technology. Hence keeping pace with electronics lead to more and more components being fabricated on single chip, hence fewer chips were needed to construct a single processor. Intel in 1971 achieved a breakthrough of putting all the components of a computer on a single chip. The single chip processor is known as a microprocessor. The Intel 4004 was the first microprocessor. It was a primitive microprocessor designed for a specific application. In Intel 8080, which came into being in 1974, was the first general-purpose microprocessor. This microprocessor was meant to be used for writing programs that could be used for general purpose computing. It was an 8-bit microprocessor. Motorola is another manufacturer in this area. At present 32 and 64 bit, general-purpose microprocessors are already in the market. Let us look into the development of most important series of microprocessors as depicted table 1.3.

Table 1.3 Microprocessor Evolution

Sl. No	Processor	Year	Memory size	Bus width	Observation
1	4004	1971	640 bytes	4 bits	Processor for specific applications
2	8080	1974	64 KB	8 bits	First general-purpose micro-processor. It was used in the development of the first personal computer
3	8086	1978	1 MB	16 bits	(i) Supported instruction, cache memory or queue (ii) Was the first powerful machine.
4	80386	1985-1988 Various version	4 GB Processor	32 bits	(i) First 32 bit (ii) The processor supports multitasking
5	80486	1989-1991	4 GB	32 bits	(i) Use of powerful cache technology. (ii) Supports pipeline based instruction execution (iii) Contain built in facility in the form of built-in math coprocessor for floating point instructions.
6	Pentium	1993-1995	64 GB	32-bits & 64 bits	Uses superscalar techniques that are execution of multiple instructions in parallel.
7	Pentium II	1997	64 GB	64 bits	Contains instructions for handling, processing of video, audio, graphics etc. This technology was MMX technology.
8	Pentium III	1999	64 GB	64 bits	Supports 3D graphics software
9	Pentium IV	2000	64 GB	64 bits	Contains instructions for enhancement of multimedia. A very powerful processor.
10	Itaium	2001	64 GB	64 bits	Supports massively parallel computing architecture.
11	Xeon	1999	64 GB	64 bits	(i) Support hyper threading. (ii) Outstanding performance and dependability: ideal for low cost servers.
12	Dual-core	2007	L2 cache	64 bits	Supports pipelining and parallel processing
13	Core-2duo	2008	L2 cache	64 bits	Better support for pipelining and parallel processing
14	Core-i3	2010	L2 cache	64 bits	Integrated memory controller supporting DDR3 in dual channel architecture.
15	Core-i5	2010	L2 cache	64 bits	Turbo boost technology
16	Core-i7	2011	L3 cache	64 bits	Support for multiple core processors enhancing the performance.

1.8 A BASIC ORGANIZATION OF COMPUTER SYSTEM: VON NEUMAN MODEL

We know that information processing, plays a very important role in taking decisions every moment. In this context, computers play a significant role in bulk processing of information. Now, we will study the organization of a computer by which it is able process the information. The computer operates on a program or set of instructions which is stored in it. We discuss the important contribution made by John Von Neumann. Who is the architect of the stored programme concept. A study of the organization of the computer helps in understanding the working concept computer. The basic organization of the computer is illustrated in figure 1.2. The following are the basic unist of a computer system.

- Input Unit
- Central Processing Unit (CPU)
- Memory Unit
- Output Unit

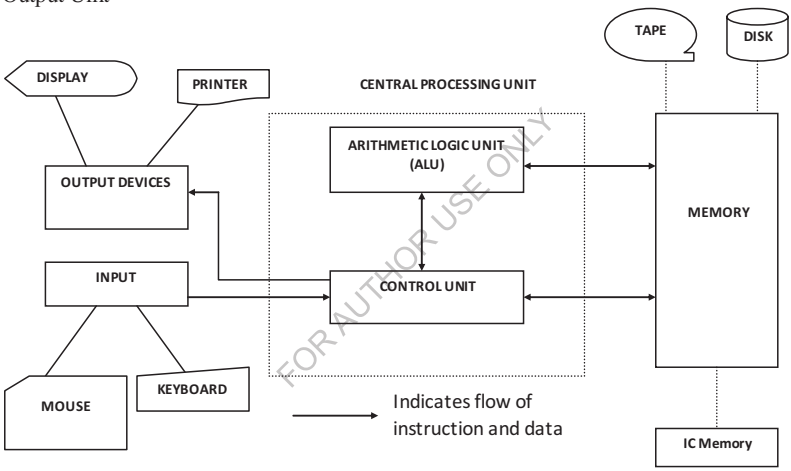


Figure.1.2 Basic Organization of the Computer System

1.8.1 Input unit

The input device is used to enter data and instructions into a computer. The devices like keyboard, mouse and scanner are commonly used as input devices. A keyboard is used to enter alphanumeric characters and symbols. The mouse is used to pick or select a command from the monitor screen. A scanner is used to scan an image or read a barcode.

1.8.2 Central Processing Unit:

The central processing unit(CPU) comprises a processor which interprets the program instructions held in memory, controls the flow of data and instructions performs arithmetic and logical operations. The program instructions are processed one at a time along with the necessary data. The results obtained are sent to memory and the next instruction is then processed. This method is repeated until all the program are executed.

Arithmetic and Logic unit:

The arithmetic and logic unit (ALU) is part of the CPU of the computer. It consist of circuits and registers which perform arithmetic (+, -, *, /) and logic (>,<,<=,>=,etc) operations.

Control unit:

The control unit controls does not perform any actual processing activity or job but it controls and coordinates the overall activities of the components of the computer. It sends commands signals to control the sequence of instructions to be executed. The control unit may be defined as "that component of the computer parts that effects the retrieval of instructions from memory in a proper sequence and thenissues proper signals to the arithmetic unit and the other components for the execution of its commands".

In short the function of the control circuitry is to interpret the instruction words and then sequence the necessary signals to those sections of the computer that will cause it to perform the instructions.

1.8.3 Memory Unit:

The memory unit is the place where all the input data, instructions and results are stored by the computer. The CPU memory is also called the memory register. The memory of a computer is also available in the form of Random Access Memory (RAM). RAM is a semiconductor chip. RAM is considered as a volatile memory; it means that as long as power is supporting the information stored in the RAM will remain in it. Once the power is lost, the information stored in the RAM also get erased. Microcomputers contain read Only Memory (ROM). ROM contains instructions for the microcomputers. Microcomputers use ROM, programmable read only memory (PROM), and erasable programmable read-only memory (EPROM) to store selected application programs. The contents of ROM are determined when the chips are manufactured. The ROM memory is considered as non volatile; it means that information does not get erased even when power has failed. The most important ROM chip(s) we should know about is the Basic Input/output System or BIOS. The BIOS is a collection of small computer programs built into a ROM chip.

1.8.4 Output Unit:

The output device is used to display or print results from a computer. Monitor, printer and plotter are the commonly used output devices. A monitor is used to display the result in the form of text and graphics. The printer is used to print the result. A plotter is used to plot or print the graphical result from a computer. Note that a result shown in a monitor is displayed temporary and it disappears when the next result is displayed, whereas the output recorded using a printer or a plotter constitutes a permanent and these printouts can be used for any business correspondence or documentation. Normally soft copy is referred to that information which is stored on the storage device. A hard copy refers to a paper print out showing the same information.

1.9 STORED PROGRAM CONCEPT

Most computers use the stored-program concept designed by the Hungarian mathematician John von Neumann. In John von Neumann architecture, a computing machine uses a single storage structure to hold both the set of instructions(on how to perform the computation) and the data required for the computation or the data generated by the computation. Such machines are also

known as stored program computers. The separation of storage from the processing unit is implicit in this model. The storage of instructions in computer memory is to enable the computer to perform a variety of tasks in sequence.

The stored program concept has the following features

(a) Random access memory stores information and it is accessible independently of its content.
(b) A central processing unit that accesses the RAM using a fetch-decode-execute cycle.
(c) Input/output devices.

The time taken to access the memory is constant over all addresses; each address stores the same amount of information.

1.10 COMPUTER HARDWARE AND SOFTWARE

A computer system consists of hardware and software. A hardware refers to any physical, electrical, mechanical or electromechnaical component of the computer. For example the input unit keyboard, mouse and output unit or even the cabinet of the computer are all considered as hardware items. A software refers to a program or a set of instructions that is written to achieve a specified task.

1.11 DEFINATION OF SOME IMPORTANT TERMS RELATED TO COMPUTERS:

Adapter: Most of the time it refers to a card that plugs into the motherboard adding special capabilities not originally found on the computer. Other times, it refers to tools to convert one connector type to another.

Cables: A thick wire that connects the computer to an external device or a power supply outlet.

Cache:An interface between the CPU and the memory (RAM and ROM). It helps the CPU keep running even though the RAM may be too slow. It does this by keeping a copy of what the processor has read/written. Card Slots found on the PC motherboard may be one of five types: ISA, EISA, MCA, VESA & PCI.. Slower adapters (like I/O boards) can be ISA. But for the best performance, we use VESA or PCI for harddrives, CD-ROMs or Video adapters.
Cards: Printed circuit board that plugs into the motherboard.

Cabinet: The cabinet, or tower case, is box contains all the parts that make the computer work.

CD-ROM: A disk made of plastic and aluminum which can store up to 650MB of data. Usually these disks cannot be written to, instead they often are used to distribute software from companies.

CPU: Central Processing Unit. The "brain" of the computer. It executes commands which, eventually, we see as a response to our input. Without the CPU, the computer is nothing.

Disk: A storage medium to keep data while the computer is turned off.DRAM or Dynamic RAM uses a device called a "capacitor" to store each bit. The problem with this is that capacitor loses the charge very quickly. Therefore, the DRAM has to be "refreshed" to keep the data valid. This is thus far the cheapest RAM.

DVD: The DVDs offer higher storage capacity than Compact Discs while having the same dimensions.

Floppy: A disk that has flexible media (the actual material onto which the data is recorded). The material and flexibility is a lot like that of a cassette tape.

Glidepoint: A mouse-replacement that has a little pad that you can use to move the mouse pointer. Simply glide your finger over the surface and the pointer will move. To "click", tap the pad. To "double-click", double-tap the pad.

Hard disk: A medium to store data for the computer when the power is switched off. It uses a hard material (typically aluminium).

Keyboard: A typewriter-like tool that has keys. Sends letters or commands to the computer.

Micro:A CPU that is composed of only one chip. Some CPUs may actually be processors several square feet is size; but the microprocessor is designed to be 100% self-contained in a single chip.

Modem: A device that will let your computer talk to other computers through the telephone line.

Monitor: The CRT or display that shows the words, graphics, etc., to the user. It is a critical part of a user's interface.

Motherboard: A printed circuit board that has (at least) slots to connect cards into. Often, they also include a CPU and memory.

Mouse: An input small hand held device that serves as an effective point-and-draw device.

Open: The original computer companies hide their secrets from competitors by Architecture keeping their architecture closed (proprietary). Feature IBM made the IBM PC an open architecture, allowing anyone to make options from it.

Parallel: A type of port which transmits and receives several bits of data at a time (typically 8 bits). Typically used to connect to printers.

Ports: Connectors (usually in the back of the computer) which connect to external devices (e.g. mouse, keyboard, modem, printer, display, etc.)

Power supply:A basic component in the computer that converts the supply power into computer can use.

Printer: An external device that takes commands and data from the computer to print the results on paper. There are several types of printers: daisy-wheel, matrix, laser, thermal, inkjet, and plotter.

RAM: "Random Access Memory". A pool of storage for the CPU. It can be written to/read from in any order (unlike a VCR tape which is serial— you have to wind to the place you want). There are several types of RAM: SRAM, DRAM, EDO-RAM.
ROM: "Read Only Memory". Memory that has imprinted in it data and programs for the CPU which cannot be erased or written to.

Scanner : An external device that is able to optically read in printed material—kind of like a copier, but it stores the image on the computer instead.

Serial : A type of port that transmits only one bit at a time. In order to send a byte of data, the data has to be "turned on its side" and send out bit by bit.

SRAM: RAM that does not "lose its mind" if not refreshed. This is typically used in caches. It tends to be much more complicated than DRAM and thus much more costly.

Surge: A device that will isolate your computer from outlet power problems (spikes and noise).

Trackball: A mouse replacement that is a small box with a ball in the center. You roll the ball in the direction you want the pointer to go.

Trackpoint : A mouse replacement with a little rubber post between the "g" and "h" keys on some laptop computers. Gently push the post in the direction you want the mouse pointer to go.

UPS : "Uninterrupted Power Supply". A battery supported power unit between the external power source and a computer system that supplies clean and continuous power even during power failures.

QUESTIONS

1) A Computer consists of --- units.
   (a) 3
   (b) 4
   (c) 5
   (d) 6
2) Keyboard is an example of ------ unit.
   a) Memory b) Input c) Output d) ALU
3) ALU stands for -------
   (a) Arithmetic Logic Unit (b) Arithmetic Lower Unit (c) Add Logical Unit
   (d) None of the above
4) RAM is considered as a ----------
   (a) Volatile Memory (b) Non volatile Memory (c) Permanent
   (d) None of the above
5) ------ contains the a program during the manufacturing itself.
   (a) RAM (b) ROM (c) Both a and b (d) None of the above
6) ------- unit is used to store information.
   (a) Input (b) Output (c) Control (d) Memory
7) In Stored program concept ---- and --- are stored in the same memory.
   (a) Data and Instruction (b) Data and Operands (c) Instruction and operation code (d) None of the above
8) Microprocessor is the heart of ------ computer.
   (a) Digital (b) Analog (c) Both a and b (d) None of the above

Answers: 1 c
2 b
3 a
4 a
5 b
6 d
7 a
8 a

EXERCISES

1. Mention the basic functional units of a computer?
2. Briefly discuss the basic anatomy of a modern computer. **[NEHU 2008]**
3. With a neat diagram explain the working organization of a computer?
4. What is stored program concept or John Von Neumann concept?
5. What is microprocessor?
6. What are the differences between RAM and ROM?

CHAPTER 2

COMPUTER ARITHMATICS AND LOGIC CIRCUITS

2.1 NUMBER SYSTEMS:

Number systems or systematic methods of representing numeric quantities which are closely related to the development and advancement in culture, science, and mathematics. Whenever we speak of numbers, most people automatically think in terms of the decimal number system, the method of counting we have used since childhood. There are dozens of number systems in use by the world today - some of which are often better suited for particular applications than the decimal system.

A computer is a device designed to the express purpose of computing in the most efficient economical manner possible. To do this the computer designers have applied their efforts and expertise. One of their conclusions reached is that it is essential to the development an efficient, economical, and reliable computer that physical quantities must be represented within the computer in forms other than in the traditional decimal number system. Therefore, since computers internally represent physical or numerical quantities in a non-decimal system, it is essential that the computer operator understand these non-decimal number systems in order that he/she may carry out his/her duties efficiently.This self-paced text introduces to the specific concepts of decimal, binary, and hexadecimal number system.

2.2 BASES:

Most people today usually represent numbers in decimal format, because we have 10 fingers to represent values. But we may also represent them in any other base that would be more convenient for a particular task. The most used bases are as follows:

Table 2.1 Number system Bases and Symbols

Name	Base	Symbols
Binary	2	0,1
Octal	8	0,1,2,3,4,5,6,7
Decimal	10	0,1,2,3,4,5,6,7,8,9
Hexadecimal	16	0,1,2,3,4,5,6,7,8,9,A,B,C,D,E,F

Table 2.2 Binary Equivalency

Bin	0000	0001	0010	0011	0100	0101	0110	0111	1000	1001	1010	1011	1100	1101	1110	1111
Oct	0	1	2	3	4	5	6	7	10	11	12	13	14	15	16	17
Dec	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15

Hex	0	1	2	3	4	5	6	7	8	9	A	B	C	D	E	F

Here, a value represented in base B as the number N will be noted as N_B. It is important to note that the numbers of a same column in the above table (14, 1110_2, 16_8 and E_{16}) correspond to the same value represented in different bases. It may compute numbers in many different bases and equal the same value but represented in different bases. For example, computers make calculus in binary but users read results in decimal whereas programmers prefer hexadecimal representation. This means that bases are normally not a concern until values are entered (keyboard) or displayed (screen, printer) into or from the computer.

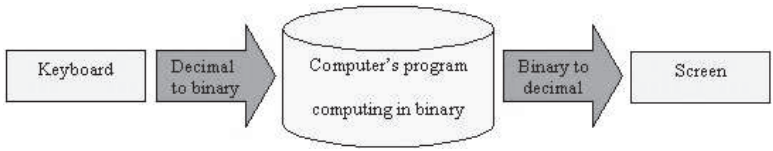


Figure 2.1 Decimal input and output after processing in binary

Computers only understand binary number ones (1) and zeros (0). Most computer programs and machine languages are coded in hexadecimal notation. This representation focus on converting decimal, binary and hexadecimal numbers since binary numbers are used to manage Internet Protocol (IP) addresses and hexadecimal numbers are used to identify Media Access Control (MAC) addresses.

2.3 DECIMAL BREAKDOWN

Numbers may be broken down into fields. Each field has a value assigned to it. Placing a valid symbol in each field changes the total value of the number.

Let's consider the decimal number 1523 (or 1523_{10}). We can break down this number into the following way: 1*1000 + 5*100 + 2*10 + 3*1. By using powers of the base we can break it down like this: $1*10^3 + 5*10^2 + 2*10^1 + 3*10^0$. In this example 1 is the most significant digit of 1523, because it is multiplied by 1000 and it is the left most digit. 3 is the least significant digit because it is only multiplied by 1 and it is the right most digit.

10^3	10^2	10^1	10^0
1000	100	10	1
1	5	2	3

10^3 X 1 = (10 x 10 x 10) x 1 = 1000 x 1 = 1000
10^2 X 5 = (10 x 10) x 5 = 100 x 5 = 500
10^1 X 2 = (10) x 2 = 10 x 2 = 20
10^0 X 3 = (1) x 3 = 1 x 3 = 3
1523

2.4 BINARY BREAKDOWN:

The smallest measurement of computer data is called a bit which can have a positive (1) or negative (0) value. Eight bits equal one byte used to represent 256 (0-255) unique characters or symbols in a computer.

Example: Character	Decimal	Binary
6	054	00110110
A	065	01000001

Let's consider the decimal number 10001100 (or 10001100_2). We can break this number down in the following way: 1*128 + 0*64 + 0*32 + 0*16 + 1*8 + 1*4 + 0*2 + 0*1. By using powers of the base we can break it down like this: $1*2^7 + 0*2^6 + 0*2^5 + 0*2^4 + 1*2^3 + 1*2^2 + 0*2^1 + 0*2^0$. In this example 1 is the most significant digit of 10001100, because it is multiplied by 128 and it is the left most digit. 0 is the least significant digit because it is only multiplied by 1 and it is the right most digit.

2^7	2^6	2^5	2^4	2^3	2^2	2^1	2^0
128	64	32	16	8	4	2	1
1	0	0	0	1	1	0	0

2^7 x 1 = (2 x 2 x 2 x 2 x 2 x 2 x 2) x 1 = 128 x 1 = 128
2^6 x 1 = (2 x 2 x 2 x 2 x 2 x 2) x 1 = 64 x 0 = 0
2^5 x 1 = (2 x 2 x 2 x 2 x 2) x 1 = 32 x 0 = 0
2^4 x 1 = (2 x 2 x 2 x 2) x 1 = 16 x 0 = 0
2^3 x 1 = (2 x 2 x 2) x 1 = 8 x 1 = 8
2^2 x 1 = (2 x 2) x 1 = 4 x 1 = 4
2^1 x 1 = (2) x 1 = 2 x 0 = 0
2^0 x 1 = (1) x 1 = 1 x 0 = 0
140

2.5 HEXADECIMAL BREAKDOWN

Computer characters may be represented by two hexadecimal symbols. Each hexadecimal symbol represents four bits, also known as a nibble. The maximum decimal value of a hexadecimal symbol is 15. Valid hexadecimal symbols are 0,1,2,3,4,5,6,7,8,9,A,B,C,D,E,F. Since 10 is a two symbol number it is replaced with an A. (A=10, B=11, C=12, D=13, E=14, F=15). The hexadecimal symbol F (or F_{16}) equals decimal 15 (or 15_{10}) (See Annex B for the full set of ASCII codes.) For example;

Character	Decimal	Hexadecimal
6	054	36
A	065	41

Let's consider the hexadecimal number BE (or BE_{16}). Since each hexadecimal symbol represents four bits, we can break this number down in the following way: B = decimal 11 or 1*8 + 0*4 + 1*2 + 1*1 and E = decimal 14 or 1*8 + 1*4 + 1*2 + 0*1. By using powers of base two, we can break it down like this: $1*2^3 + 0*2^2 + 1*2^1 + 1*2^0$ and $1*2^3 + 1*2^2 + 1*2^1 + 0*2^0$. In this example B is the most significant digit of BE, because it is the left most digit. E is the least significant digit because it is the right most digit.

2^3	2^2	2^1	2^0	2^3	2^2	2^1	2^0
8	4	2	1	8	4	2	1
1	0	1	1	1	1	1	0
11				14			
B				E			

2^3 x 1 = (2 x 2 x 2) x 1 = 8 x 1 = 8
2^2 x 1 = (2 x 2) x 1 = 4 x 0 = 0
2^1 x 1 = (2) x 1 = 2 x 1 = 2
2^0 x 1 = (1) x 1 = 1 x 1 = 1
11 = B

2^3 x 1 = (2 x 2 x 2) x 1 = 8 x 1 = 8
2^2 x 1 = (2 x 2) x 1 = 4 x 1 = 4
2^1 x 1 = (2) x 1 = 2 x 1 = 2
2^0 x 1 = (1) x 1 = 1 x 0 = 0
14 = E

2.6 DECIMAL TO BINARY CONVERSION

1. We will use the following scale method to convert a decimal number to its binary equivalent.

2^{11}	2^{10}	2^9	2^8	2^7	2^6	2^5	2^4	2^3	2^2	2^1	2^0
2048	1024	512	256	128	64	32	16	8	4	2	1

The above scale may be used to convert the decimal numbers 0-4095. For example, we could convert the decimal number 1024 to a binary number by simply turning on the 1024 column with a one and turning off the rest of the columns with a zero.

2^{11}	2^{10}	2^{9}	2^{8}	2^{7}	2^{6}	2^{5}	2^{4}	2^{3}	2^{2}	2^{1}	2^{0}
2048	1024	512	256	128	64	32	16	8	4	2	1
0	1	0	0	0	0	0	0	0	0	0	0

Decimal 1024 = Binary 10000000000
(Note: 1 kilo bits (Kb) really equals 1024 bits not 1000 bits)

2. Since computer data and IP addresses are measured in Bytes, we only need eight bits to convert the decimal numbers 0-255. You do not need to know how to convert base 2 numbers to their decimal equivalent if you can remember the numbers 1,2,4,8,16,32,64 and 128. (**1**x2=**2**x2=**4**x2=**8**x2=**16**x2=**32**x2=**64**x2=**128**) We will use the following scale to convert decimal numbers 0-255.

128	64	32	16	8	4	2	1

Decimal number 255 is equivalent to binary number 11111111 when we turn on all eight bits.

128	64	32	16	8	4	2	1
1	1	1	1	1	1	1	1

3. Now let's convert decimal number 145 to its binary equivalent.
a. First find the number on the scale closest to 145, without going over it and place a one directly below the number on the scale.

128	64	32	16	8	4	2	1
1							

b. Now take the number that you located on the scale closest to 145 (which is 128) and subtract it from 145.

$$\begin{array}{r} 145 \\ -\ 128 \\ \hline 17 \end{array}$$

c. Next locate the number 17 on the scale or the one closest to it without going over and place a one (1) directly below the number on the scale.

128	64	32	16	8	4	2	1
1			1				

d. The number that came close to 17 was the number 16 on the scale. Subtract the number from 17 and you should come up with the number 1.

$$\begin{array}{r} 148 \\ -\ 128 \\ \hline 17 \\ -\ 16 \end{array}$$

1

e. Now, locate the number 1 on the scale and place a binary 1 under that number.

128	64	32	16	8	4	2	1
1			1				1

f. Any blanks space on the scale to the right of the left most significant digit will be filled in with zeros.

128	64	32	16	8	4	2	1
1	0	0	1	0	0	0	1

g. You now have the binary equivalent to decimal 145

Decimal 145 = Binary 10010001

2.7 BINARY TO DECIMAL CONVERSION

1. Convert a binary number to a decimal number is just the opposite to converting a decimal number to a binary number.
2. We will use the scale method to convert binary number 101101 to its decimal equivalent.

2048	1024	512	256	128	64	32	16	8	4	2	1

a. The first step is to plug in the binary numbers on the scale starting from right to left (right justified).

2048	1024	512	256	128	64	32	16	8	4	2	1
						1	0	1	1	0	1

b. Then we take the decimal number above the binary ones (1) and add them together to get the decimal equivalent.

$$\begin{array}{r} 32 \\ 8 \\ 4 \\ +\,1 \\ \hline 45 \end{array}$$

c. Binary 101101 = Decimal 45

3. The following illustration proves that binary number 101110111000 equals decimal number 3000.

2048	1024	512	256	128	64	32	16	8	4	2	1
1	0	1	1	1	0	1	1	1	0	0	0

2048
512
256
128
32
16
+ 8
3000

2.8 HEXADECIMAL TO BINARY

1. The hexadecimal number system uses base 16 (decimal = base 10 and binary = base 2). Since the decimal system provides only ten digits to represent the first ten values of the hexadecimal system (0-9), the remaining six hexadecimal values are arbitrarily represented by the first six letters of the alphabet: A, B, C, D, E, and F. Thus, the entire symbolic set of the hexadecimal number system consists of 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, A, B, C, D, E, and F.

Dec	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Hex	1	2	3	4	5	6	7	8	9	A	B	C	D	E	F

2. A hexadecimal digit represents a fixed set of four bits or binary digits:

Example: Hexadecimal A = Binary 1010

3. The conversion to and from binary is relatively simple. Hexadecimal to binary is made by replacing each hexadecimal digit by the equivalent set of four binary digits. To illustrate, Hexadecimal number E7A is converted to binary.

Dec	1	2	3	4	5	6	**7**	8	9	**10**	11	12	13	**14**	15
Hex	1	2	3	4	5	6	**7**	8	9	**A**	B	C	D	**E**	F
Bin	0001	0010	0011	0100	0101	0110	**0111**	1000	1001	**1010**	1011	1100	1101	**1110**	1111

Hexadecimal E = Decimal 14 = Binary 1110

Hexadecimal 7 = Decimal 7 = Binary 0111

Hexadecimal A = Decimal 10 = Binary 1010

E7A = 111001111010

4. Each hexadecimal digit must be converted individually and you must use all four binary digits to represent a hexadecimal number even though you may have left zeros:

Example: Hexadecimal 1 = Binary 0001

5. We will now convert the hexadecimal number 5CB to a binary number using the scale method.

a. To convert multiple hexadecimal characters you must first convert each character to its decimal equivalent.

Dec	5	12	11
Hex	5	C	B

b. Next, convert each decimal digit to a four bit binary number.

	8	4	2	1	8	4	2	1	8	4	2	1
Bin	0	1	0	1	1	1	0	0	1	0	1	1
Dec	5				12				11			
Hex	5				C				B			

c. The last step is to combine al 4-bit binary numbers.

Hexadecimal 5 = Binary 0101

Hexadecimal C = Binary 1100

Hexadecimal B = Binary 1011

Hexadecimal 5CB = Binary 010111001011

2.9 HEXADECIMAL TO DECIMAL

1. To convert a hexadecimal number to its decimal equivalent, simply convert the hexadecimal number to its binary equivalent and then from binary to decimal.

2. We will use the following scale to convert hexadecimal 7B2 to decimal 1970.

	2048	**1024**	**512**	**256**	**128**	**64**	**32**	**16**	**8**	**4**	**2**	**1**
	8	**4**	**2**	**1**	**8**	**4**	**2**	**1**	**8**	**4**	**2**	**1**
Bin												
Dec												
Hex												

a. The first step is to place each hexadecimal character in its own 4-bit column.

	2048	**1024**	**512**	**256**	**128**	**64**	**32**	**16**	**8**	**4**	**2**	**1**
	8	**4**	**2**	**1**	**8**	**4**	**2**	**1**	**8**	**4**	**2**	**1**
Bin												
Dec												
Hex	7				B				2			

b. Next convert each hexadecimal character to its decimal equivalent.

	2048	**1024**	**512**	**256**	**128**	**64**	**32**	**16**	**8**	**4**	**2**	**1**
	8	**4**	**2**	**1**	**8**	**4**	**2**	**1**	**8**	**4**	**2**	**1**
Bin												
Dec	7				11				2			
Hex	7				B				2			

c. Now convert each decimal number to a 4-bit binary number.

	2048	1024	512	256	128	64	32	16	8	4	2	1
	8	4	2	1	8	4	2	1	8	4	2	1
Bin	0	1	1	1	1	0	1	1	0	0	1	0
Dec	7				11				2			
Hex	7				B				2			

d. The last step is to convert the combined binary digits (011110110010) to its decimal equivalent like you were taught in a previous section.

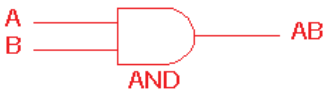
1024
512
256
128
32
16
+ 2
1970

Hexadecimal 7B2 = Binary = 011110110010 = Decimal 1970

2.10 LOGIC GATES

Digital systems are said to be constructed by using logic gates. The basic gates are the AND, OR, NOT gates. The basic operations are described below with the aid of tables in the following, called truth tables.

2.10 .1 AND gate



2 Input AND gate		
A	B	A.B
0	0	0
0	1	0
1	0	0
1	1	1

The AND gate is an electronic circuit that gives a **high** output (1) only if **all** its inputs are high. A dot (.) is used to show the AND operation i.e. A.B. Bear in mind that this dot is sometimes omitted i.e. AB

2.10 .2 OR gate

2 Input OR gate		
A	B	A+B
0	0	0
0	1	1
1	0	1
1	1	1

The OR gate is an electronic circuit that gives a high output (1) if **one or more** of its inputs are high. A plus (+) is used to show the OR operation.

Truth table for AND,

A	B	Z
0	0	0
0	1	0
1	0	0
1	1	1

Z=A.B

Switch realisation of AND:

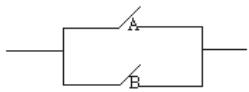
Continuity occurs only when both A AND B are closed.

Truth table for OR,

A	B	Z
0	0	0
0	1	1
1	0	1
1	1	1

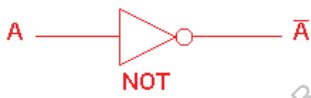
Z=A+B

Switch realisation of OR:



Continuity if A or B or both are closed.

2.10 .3 NOT gate



NOT gate	
A	$\bar{A}$
0	1
1	0

The NOT gate is an electronic circuit that produces an inverted version of the input at its output. It is also known as an *inverter*. If the input variable is A, the inverted output is known as NOT A. This is also shown as A', or A with a bar over the top, as shown at the outputs.

2.10 .4 EXOR gate

2 Input EXOR gate		
A	B	A⊕B
0	0	0
0	1	1
1	0	1
1	1	0

The '**Exclusive-OR**' gate is a circuit which will give a high output if **either, but not both**, of its two inputs are high. An encircled plus sign (⊕) is used to show the EOR operation.

2.11 SIMPLE BINARY ADDER (HALF ADDER)

A key requirement of digital computers is the ability to use logical functions to perform arithmetic operations. The basis of this is addition; if we can add two binary numbers, we can just as easily subtract them, or get a little fancier and perform multiplication and division. How, then, do we add two binary numbers?

Let's start by adding two binary bits. Since each bit has only two possible values, 0 or 1, there are only four possible combinations of inputs. These four possibilities, and the resulting sums, are:

0 + 0 = 0
0 + 1 = 1
1 + 0 = 1
1 + 1 = 10

Whoops! That fourth line indicates that we have to account for two output bits when we add two input bits: the sum and a possible carry. Let's set this up as a truth table with two inputs and two outputs, and see where we can go from there.

INPUTS		OUTPUTS	
A	**B**	**CARRY**	**SUM**
0	0	0	0
0	1	0	1
1	0	0	1
1	1	1	0

Well, this looks familiar, doesn't it? The Carry output is a simple AND function, and the Sum is an Exclusive-OR. Thus, we can use two gates to add these two bits together. The resulting circuit is shown below.

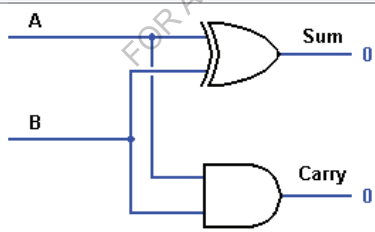


Figure 2.2: Diagram of binary adder

2.12 SET – RESET (SR) FLIP FLOP

"Flip-flop" is the common name given to two-state devices which offer basic memory for sequential logic operations. Flip-flops are heavily used for digital data storage and transfer and are commonly used in banks called "registers" for the storage of binary numerical data.
The SRFF (Set – Reset Flip Flop) can be constructed of two NOR gates plus feedback as shown in the circuit diagrams below. In this SRFF both set and reset cannot be 1 as it generates an unstable state.

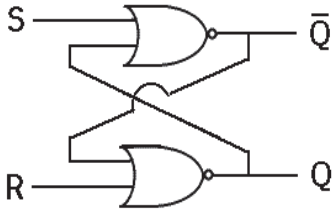


Figure 2.3 : SR Flipflop

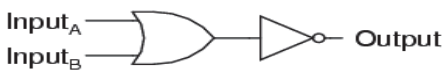
S	R	Q	Q'
1	0	1	0
0	0	1	0
0	1	0	1

Here looking at the table we see that The output Q still keeps its value unchanged when S is switched from 1 to 0 and it only changes when R is made 1 or Reset. This is how basic memory units work.

2-input NOR gate

A	B	Output
0	0	1
0	1	0
1	0	0
1	1	0

Equivalent gate circuit



2.13 MULTIPLEXER

This is a digital circuit with multiple signal inputs, one of which is selected by separate address inputs to be sent to the single output. It's not easy to describe without the logic diagram, but is easy to understand when the diagram is available.

A two-input multiplexer is shown below.

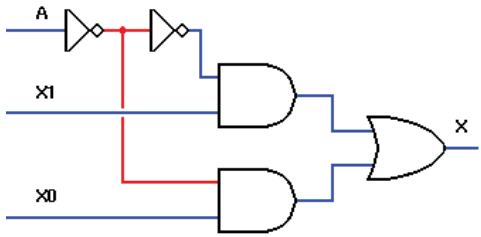


Figure 2.4 A two-input multiplexer

The multiplexer circuit is typically used to combine two or more digital signals onto a single line, by placing them there at different times. Technically, this is known as *time-division multiplexing*.

Input A is the addressing input, which controls which of the two data inputs, X0 or X1, will be transmitted to the output. If the A input switches back and forth at a frequency more than double the frequency of either digital signal, both signals will be accurately reproduced, and can be separated again by a *demultiplexer* circuit synchronized to the multiplexer.

This is not as difficult as it may seem at first glance; the telephone network combines multiple audio signals onto a single pair of wires using exactly this technique, and is readily able to separate many telephone conversations so that everyone's voice goes only to the intended recipient. With the growth of the Internet and the World Wide Web, most people have heard about T1 telephone lines. A T1 line can transmit up to 24 individual telephone conversations by multiplexing them in this manner.

2.13 DEMULTIPLEXER

The opposite of the multiplexer circuit, logically enough, is the *demultiplexer*. This circuit takes a single data input and one or more address inputs, and selects which of multiple outputs will receive the input signal. The same circuit can also be used as a *decoder*, by using the address inputs as a binary number and producing an output signal on the single output that matches the binary address input. In this application, the data input line functions as a circuit enabler — if the circuit is disabled, no output will show activity regardless of the binary input number.

A one-line to two-line decoder/demultiplexer is shown below.

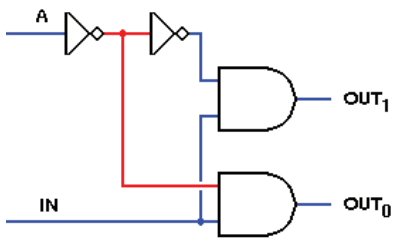


Figure 2.5: A demultiplexer

This circuit uses the same AND gates and the same addressing scheme as the two-input multiplexer circuit shown in these pages. The basic difference is that it is the inputs that are combined and the outputs that are separate. By making this change, we get a circuit that is the inverse of the two-input multiplexer.

EXERCISES

1. What is number system? Describe various number systems.
2. Convert $(17.35)_{10}$ to binary number and $(10101.10101)_2$ to decimal number. **[NEHU 2008]**
3. What is Universal Gate? Show that NAND gate is a Universal Gate. **[NEHU 2008]**
4. Convert $(25)_8$ to binary number and $(100111.10101)_2$ to octal number.
5. Convert $(53E)_{16}$ to binary number and $(10011101)_2$ to hexadecimal number.
6. Convert $(A17)_{16}$ to decimal number.
7. Convert $(67)_8$ to hexadecimal number.

CHAPTER 3

INPUT AND OUTPUT UNIT

3.1 INPUT AND OUTPUT UNIT

3.1.1 Input unit:

The input device is used to enter data and information into a computer. The devices like keyboard, mouse and scanner are commonly used as input devices. A keyboard is used to enter alphanumeric characters and symbols. The mouse is used to click or select a icons and shortcuts from the monitor screen. A scanner is used to scan an image, documents and so on.

3.1.2 Output Unit:

The output device is used to display or print results from a computer. Monitor, printer, speaker and plotter are commonly used output devices. A monitor is used to display the result in the form of text and graphics. The printer is used to print the results. A plotter is used to plot or print graphical result from a computer. Note that a result displayed in a monitor is temporary and it disappears when the next result is displayed, whereas the output printed using a printer or a plotter is permanent and these printouts can be used for any business correspondence or documentation. Normally soft copy is referred to the information that is stored on the storage device. A hard copy refers to a print out showing the information.

3.2 INPUT DEVICES

3.2.1 Keyboard:

A keyboard is an input device used to enter data into a computer. The Keyboard layout is known as the QWERTY design it is connected to the machine through serial port or USB plugs. The keyboard usually contains function keys, numeric keys and toggle keys (caps lock, num lock, scroll lock) and so on. A keyboard is used to enter data into a computer. The keyboard contains function keys, numeric keys and toggle key (Caps lock, Num lock, Scroll lock) and so on.

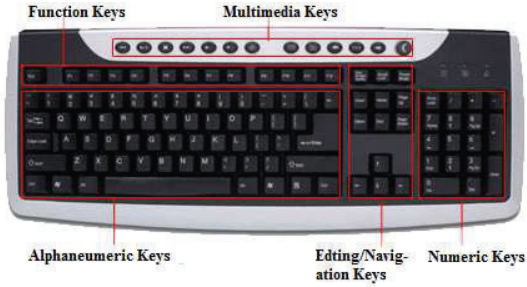


Figure 3.1. A keyboard with various parts.

It is the most widely used input device. it has keys similar to a typewriter to enter characters and other symbols. The function keys are used to activate a particular feature of software like invoking the help system, selecting a menu and so on.

There is a separate numeric keypad to enter numeric keypad to enter numeric data. When a key is pressed the electric circuitry under the key will change which will be detected by the microprocessor and the binary code for the character is sent to the CPU. Some keyboards have a temporary memory or buffer to store the information typed a little ahead of the need of the computer.

3.2.2 Mouse:

A mouse is an input device used to controls the movement of the cursor or pointer on a display screen.

Figure 3.2. A mouse.

The cursor is moved to the required icon or menu on the monitor and a button is pressed. The control is sent to the CPU to select the command corresponding to the icon or menu item. The latest is the wireless mouse or remote mouse which works on transmission of infrared or radio waves to communicate with the computer.

The mouse can also be used to open menus, select text for editing, move objects on the screen and draw images or diagrams. There are three basics type of mouse such as mechanical, optomechanical and optical mouse. The mechanical mouse uses a rubber-coated ball on the underside and it can roll in every direction. The movement of this ball sends electrical signals to the system unit which causes the cursor or pointer to move in a corresponding fashion. An optomechanical same as the mechanical mouse except that it uses optical sensors to the motion of the ball.The optical mouse do not have any mechanical moving parts as it uses diodes to emit light onto a metal pad performing the same work but with great accuracy.

3.2.3 Scanners:

A scanner is a device that scans documents such as photographs and pages of text to computer storage devices. When a document is scanned, it is converted into a digital format. This creates an electronic version of the document that can be viewed and edited on a computer. Scanners are used to scan a printed page or an illustration. These data are then converted into bit patterns for processing storage or output. When an image is scanned, it is converted into light and dark picture elements or pixels. The scanned images are used for word processing and printing multiple copies. Scanners are also useful to scan fingerprints. The scanned fingerprints can be compared with another fingerprint to find probable match in investigative services. Photoelectric scanners are commonly used in supermarkets to read barcodes.

Figure 3.3. Diagram of Scanners.

Scanners are available in different sizes. A handheld scanner is used to scan a few lines of text or a small photograph. A page scanner is used to scan a drawing or page.The scanner is connected to the computer using a cable and controlled by software.

3.3 OUTPUT DEVICES:

Some definations:

1. **Hard copy:**

The data consisting of text or graphics that is obtained as printouts or microfilm using printers or plotters is known as hardcopy.For example, the hardcopy of an engineering drawing is obtained using plotters. Some hardcopy devices include dot matrix printer, laser printer, inkjet printer , flatbed pen plotter and drum type inkjet plotter. A combination of printing, scanning, copying and/or faxing can also obtain a hardcopy. A hardcopy can be used for business correspondence and documentation. A copier machine also comes under hardcopy devices.

2. **Soft copy:**

The soft copy is the unprinted digital document file.The data that is stored in a storage device such as floppy disk, hard disk, CD-ROM magnetic tape and so on is called softcopy.The data in a softcopy may be modified using the relevant software. A few softcopy devices are monitor and pendrive.

3. **Input/Output Ports:**

(a) USB

The basic USB has trident logo each release has specific variation. USB was designed to standardize the connection of computer peripherals, such as keyboards, pointing devices, digital cameras, printers, portable media players, disk drives and network adapters to personal computers, both to communicate and to supply electric power. USB replaces all the different kinds of serial and parallel port connectors with one standardized plug and port combination. The USB 2.0 specification extends the maximum speed of the connection from 12 Mbps on USB 1.1 up to 480 Mbps (60MBytes/sec). This enables the transfer of 1920x1080 images at 24fps (frames per second) for high-definition video conferencing or 320x240 images at 500fps for high speed video motion analysis.

Figure 3.4. Trident logo of USB

(b) IEEE 1394

IEEE 1394 is serial bus architecture for high-speed data transfer. IEEE 1394, also known as FireWire, is a component originated from Apple which, like USB, allows the connection of peripherals to a computer, such as video cameras. However, there is one distinct difference: IEEE 1394 supports much higher bandwidth than USB.

Figure 3.5. An IEEE Ethernet Cable

Differences between USB and IEEE 1394

Besides providing a higher bandwidth solution as compared to USB, IEEE 1394 has someadvantages and disadvantages. For one, IEEE 1394 can support only up to 63 devices hookedupvia a daisy chain, while USB can support 127 devices hooked up to a USB hub. IEEE1394,however, functions through a peer-to-peer network structure.

3.3.1 Printers:

A printer is an output device used to print text or graphics on paper or on any other hardcopy medium which includes even microfilm. A permanent copy from the computer is produced using the printer. Printers are of two basic types impact and non-impact.

Impact and Non-impact printers:

Printers are categorized based on the physical contact of the print head with the paper to produce a text or an image. An impact printer is one where the print head will be in physical contact with the paper. In a non–impact printer, on the other hand the print head will have no physical contact with the paper. The Dot matrix printer is considered as a Impact printer and Laser printer is considered as Non-impact printer.

The basic operations performed by a printer are:

1) Moving the paper to a given line.
2) Moving the print head along the line.
3) Generating the character or image.
4) Producing the character or image on the paper.

3.3.3 Dot Matrix Printer:

The most popular kind of printer for small computers is the dot matrix printer, which forms characters as arrays of dots. Dot matrix printers are compact, reliable and relatively fast. This type of printer is an impact printer. The print head is the important hardware which produces the character using pins arranged in a matrix form. Normally a print head has 9 pins or 24 pins arranged in a matrix form. Combinations of pins strike an ink bed ribbon during the printing process. The print head moves in a line and the pattern of dots required for each character is printed on the paper. After printing a line, the paper rolls to print the next line.

Figure 3.6. A dot matrix printer.

Dot matrix printers produce average quality prints and as generally used in business applications. They are used printing train number, seat number etc on a railway reservation ticket. The speed of printing in dot matrix printer in dot matrix is measured in characters per second (cps).The advantages in this type of printer is carbon copies can be obtained as printing takes place by physical impact with the paper. It is less of cost and easy to maintain.The disadvantage is average printing quality and printer ribbon printer ribbon needs to be changed frequently.

3.3.4 Laser Printer:

Laser printers are fastest type of non impact electrostatic printers. They produce high quality prints at high speeds. It operates like a copier machine. In these printers, the controlled beam of intense laser forms images on an electrically charged rotating drum. The drum is rotated near the fine black powder called the toner. These charged images which sticks to the paper due to pressure and heat. The toner consists of oppositely charged ink particles which stick to the drum in the places where the laser has charged.

Figure 3.7. A laser printer.

The light beam strikes a multi-sided rotating mirror. As the mirror rotates, the side currently in the path of the light beam sweeps the beam across the surface of the drum. As the beam sweeps across the drum, the light is modulated and a single line is drawn after a line has been drawn, the next side of the mirror is in place and a new line is drawn below the previous line.

The quality of the printout is measured by the number of dots per inch (dpi). Since the dots are printed closely, the text or graphics appears very smooth and elegant. The speed is measured in number of pages printed per minute (PPM) which varies between 5 and 25.

The advantages are good quality printouts can be obtained for documentation and business applications. The printing is faster and easy to handle and maintain. The disadvantages are the price is high and higher print cost.

3.3.5 Inkjet printer:

An inkjet is a non impact printer. It sprays tiny drops of ink to form character and graphic images on paper. The text and graphics printed in an inkjet printer are technically similar to that of a dot matrix printer. These type of printers can also be used color printing. The black inkjet printer uses black cartridge filled with black ink whereas the color printer uses four color cartridges namely cyan (blue), magenta (red), yellow and black. These four colors are used in combination to generate any color in the visible spectrum.

The print heads move across the page by the control of software and spray the dots of ink with the required combination of colors. The printer sends electrical pulses to thin resistors at the base of firing chambers behind the nozzle. A thin layer of ink is heated by the resistor which in turn forms a vapour bubble and the expansion forces ink through the nozzle and onto the paper at a rate of about 6000 dots per second. The quality of the printout is equivalent to that of laser printouts. The speed of printing is slower than that of laser printers.

The advantages of this type printer are the cost is low; quality of printing is equivalent to that of laser printing, color printouts are cheaper easy to handle and maintain.The disadvantages are the ink cartridges may get spoiled if unused for a long time. Some inkjet printers are very expensive.

3.3.6 Plotters:

A plotter is an output device used to print engineering drawing or graphics on large size sheets. These are also used to draw the patterns from which microprocessors, memory chips, and other integrated circuits are manufactured. Plotters are used when highest quality and greatest accuracy are required.

Figure 3.8. A Plotter.

There are two basic types of plotters: flat bed plotters and drum type plotters. Pen plotter is an example of a flatbed plotter. Laser plotter and inkjet plotter are commonly used drum type plotters.A pen plotter has a surface where the paper or drawing sheet is properly fixed. It has a pen holder in a movable arm. Under the control of the computer the arm with the pen moves across the paper to draw the picture. A few pens are also placed in a row and the arm will pick the required color pen as per the instruction of the computer.A drum type plotter uses a drum where the paper will be rolled. It has a print head/pen that moves like the print head in a printer. Drum type plotters are capable of producing longer, continous drawings. Drum type plotters that can produce color plots are available.The disadvantages are these are expensive than printers. The cost of printing is high. Cost of maintenance is high. High skill of operation is required. Process time of printing is longer.

QUESTIONS

1. ---- and ---- are examples of input device.
2. Printout of a program is considered as ------.
3. Payroll program stored on CD is considered as ----.
4. Dot matrix printer is an example of --------.
5. Laser printer is an example of -----.
7. The speed of Dot matrix printer is expressed as ----.
8. The speed of Laser printer is expressed as ----.

Answers:

1. Keyboard, Mouse
2. Hardcopy
3. Softcopy
4. Impact printer
5. Non-impact
6. Characters per second (CPS)
7. Pages per Minute (PPM)

EXERCISE

1. What is the difference between impact and non impact printer?
2. What is the difference between Hard and soft copy?
3. List and explain any two input and output devices.
4. With a neat diagram explain the working of a mouse.
5. What is a plotter? How plotter works?

CHAPTER 4

CENTRAL PROCESSING UNIT

4.1 CENTRAL PROCESSING UNIT:

The processing unit comprises a processor which interprets the program instructions in memory, controls the flow of data and performs arithmetic and logical operations. The program instructions are processed one at a time along with the necessary data. The results are sent to memory and the next instruction is processed. This method is repeated until the program is executed.

4.1.1 Arithmetic and Logic unit:

The arithmetic-logic unit (ALU) is the unit of the computer that performs arithmetic and logical operations on the data. This section of the machine can be relatively small consisting of circuits and registers which perform arithmetic (+, -, *, /) and logic (>,<,<=,>=,etc) operations. Arithmetic-logic units which can add and subtract and perform logical operations form the backbone for the arithmetic and control operations in computers. To perform scientific calculations the floating-point number system is used.

4.1.2 Control unit:

The control unit controls the overall component activities of the computer. It is mainly used to coordinate the activities among other units. It will send commands signals and controls the sequence of instructions to be executed. The control unit may be defined as “the parts that effect the retrieval of instructions in proper sequence and application of the proper signals to the arithmetic unit and the other parts”.

The function of the control circuitry in a general purpose computer is to interpret the instruction words and then sequence the necessary signals to those sections of the computer that will cause it to perform the instructions.

4.2 PERFORMANCE MEASURES:

In this section, we consider the important issue of assessing the performance of a computer. In particular, we focus our discussion on a number of performance measures that are used to assess computers. Let us admit at the outset that there are various facets to the performance of a computer. For example, a user of a computer measures its performance based on the time taken to execute a given job (program). On the other hand, a laboratory engineer measures the performance of his system by the total amount of work done in a given time. While the user considers the program execution time a measure for performance, the laboratory engineer considers the throughput a more important measure for performance. A metric for assessing the performance of a computer helps comparing alternative designs.

Performance analysis should help answering questions such as how fast can a program be executed using a given computer? In order to answer such a question, we need to determine the time taken by a computer to execute a given job. We define the clock cycle time as the time between two consecutive rising (trailing) edges of a periodic clock signal //(Fig. 1.1). Clock cycles allow counting unit computations, because the storage of computation results is synchronized with rising (trailing) clock edges. The time required to execute a job by a computer is often expressed in terms of clock cycles.

We denote the number of CPU clock cycles for executing a job to be the cycle count (CC), the cycle time by CT, and the clock frequency by f = 1/CT. The time taken by the CPU to execute a job can be expressed as
CPU time =CC×CT = CC/f

It may be easier to count the number of instructions executed in a given program as compared to counting the number of CPU clock cycles needed for executing that program. Therefore, the average number of clock cycles per instruction (CPI) has been used as an alternate performance measure. The following equation shows how to compute the CPI.

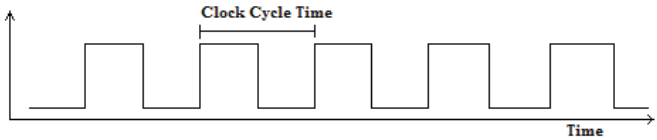


Fig. 4.1 Clock signal

CPI = (CPU clock cycles for the program)/(Instruction count)
CPU time = Instruction count × CPI × Clock cycle time
=(Instruction count × CPI)/ Clock rate

It is known that the instruction set of a given machine consists of a number of instruction categories: ALU (simple assignment and arithmetic and logic instructions), load, store, branch, and so on. In the case that the CPI for each instruction category is known, the overall CPI can be computed as

CPI=(∑CPI×I)/(Instruction Count)

where I is the number of times an instruction of type is executed in the program and CPI is the average number of clock cycles needed to execute such instruction.

Example: Consider computing the overall CPI for a machine A for which the following performance measures were recorded when executing a set of benchmark programs. Assume that the clock rate of the CPU is 200 MHz.

Instruction category	Percentage of occurrence	No. of cycles per instruction
ALU	38	1
Load & store	15	3
Branch	42	4
Others	5	5

Assuming the execution of 100 instructions, the overall CPI can be computed as
CPI=(∑CPI×I)/(Instruction Count)=(38×1+15×3+42×4+5×5)/100 = 2.76

It should be noted that the CPI reflects the organization and the instruction set architecture of the processor while the instruction count reflects the instruction set architecture and compiler technology used. This shows the degree of interdependence between the two performance parameters. Therefore, it is imperative that both the CPI and the instruction count are considered in assessing the merits of a given computer or equivalently in comparing the performance of two machines.

A different performance measure that has been given a lot of attention in recent years is MIPS (million instructions-per-second (the rate of instruction execution per unit time)), which is defined as

MIPS = (Instruction count)/ Execution time ×10^6
=(Clock Rate)/(CPI×10^6)

Example: Suppose that the same set of benchmark programs considered above were executed on another machine, call it machine B, for which the following measures were recorded.

Instruction category	Percentage of occurrence	No. of cycles per instruction
ALU	35	1
Load & store	30	2
Branch	15	3
Others	20	5

What is the MIPS rating for the machine considered in the previous example(machine A) and machine B assuming a clock rate of 200 MHz?

CPIa= (∑CPI×I)/(Instruction Count)=(38×1+15×3+42×4+5×5)/100 = 2.76
MIPSa=(Clock Rate)/(CPIa×10^6)=(200×10^6)/(2.76×10^6)=70.24
CPIb= (∑CPI×I)/(Instruction Count)=(38×1+30×2+20×5+15×3)/100 = 2.4
MIPSb=(Clock Rate)/(CPIa×10^6)=(200×10^6)/(2.4×10^6)=83.67
Thus MIPSb > MIPSa.

It is interesting to note here that although MIPS has been used as a performance measure for machines, one has to be careful in using it to compare machines having different instruction sets. This is because MIPS does not track execution time.

EXERCISES

1. Explain different parts of CPU.

2. Describe different CPU performance measurement parameters.

3. Consider computing the overall CPI for a machine A for which the following performance measures were recorded when executing a set of benchmark programs. Assume that the clock rate of the CPU is 200 MHz. Calculate the CPI.

Instruction category	Percentage of occurrence	No. of cycles per instruction
ALU	36	1
Load & store	17	3
Branch	40	4
Others	7	5

4. Suppose that the same set of benchmark programs considered in exercise were executed on another machine, call it machine B, for which the following measures were recorded.

Instruction category	Percentage of occurrence	No. of cycles per instruction

ALU	30	1
Load & store	36	2
Branch	14	3
Others	20	5

What is the MIPS rating for the machine considered in the previous example(machine A) and machine B assuming a clock rate of 200 MHz?

CHAPTER 5

MEMORY UNIT

5.1 MEMORY HIERARCHY

The memory unit is an essential component in any digital computer, because it is needed for storing programs and data. The memory hierarchy system consists of all storage devices employed in a computer system from the slow but high capacity secondary memory to a relative faster main memory. Consider the figure 5.1 to illustrate the components in a typical memory hierarchy.

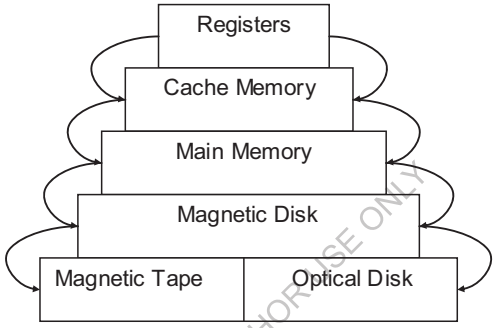


Figure 5.1: Memory Hierarchy

From the top to bottom the cost of memory will decrease and the accessing speed also decrease. But from bottom to top the storage capacity will decrease and accessing speed will increase.

Registers

Registers are fastest of all memories; a register is a group of flip-flops with each flip-flop capable of storing one bit of information. An n-bit register has a group of flip-flops and is capable of storing any binary information of bits.

Cache memory

Cache is a special very-high-speed memory. It is the intermediate memory between CPU and main memory .The cache is used for storing segments of programs currently being executed by the CPU and temporarily stored data, frequently needed in the present calculations.

Main memory

The memory unit that communicates directly with CPU is called the main memory. The main memory is a relatively large and faster memory used to store programs and data during the processor execution. The principle technology used for the main memory is based on semiconductor integrated circuits (RAM Chips). It is a volatile memory, it means the stored information remains valid as long as power is applied to the unit.

Magnetic disk

Devices that provide backup storage are called "auxiliary memory' or 'secondary memory '. The most common auxiliary memory used in computer systems are magnetic disks. They are used for storing system programs, large data files, and other backup information.

Magnetic tapes

Magnetic tapes are slow devices compare to magnetic disks, generally tapes are used for backup storage.

Optical disks

In recent years, optical disks (DVD-ROMS,) are become available. They have much higher recording density than magnetic disks. A DVD is prepared by using a high power infrared laser beam to burn 0.8 micron diameter holes on a coated glass master disk .The burned area is called pits and the un-burned areas between the 'pits' are called 'lands'. Consider the figure 1.9 it shows the memory hierarchy in a computer system.

5.2 STORAGE DEVICES INTRODUCTION

We discussed in chapter 1, memory is used for storage purpose. Microprocessor fetches instruction or the operation code from the memory. Once the operation code is decoded, it fetches operand that is followed in the memory. There are two types of memory, one is called volatile memory and other is non-volatile memory. In volatile memory, information is retained as long as power is supplied to the chips. In nonvolatile memory, information is retained, even though power is not supplied. Random access memory belongs to volatile memory and hard disk belongs to the nonvolatile memory. In this chapter we discuss, various storage devices in detail.

5.3 PRIMARY STORAGE:

RAM and ROM are both different types of memories used in any computer to make it fast and to enable it to access the information stored in the computer.

a)RAM (Random Access Memory)-

All the process executed acesses processor from RAM till the power is on. It is a volatile memory.

b)ROM (Read Only Memory)-

ROM is a CMOS chip which is integrated in the motherboard and used to store software called BIOS (Basic Input Output System)

BIOS is used to detect all the hardware present in the computer during startup process of the computer by POST (Power On Self Test). It validates the PC's hardware configuration.

Difference between RAM and ROM-

RAM	ROM
1) Used for storing data temporarily	1) Used for storing data permanently
2) RAM is volatile memory	2) ROM is non-volatile memory
3) Expensive	3) Cheaper
4) Used to hold the process at the time of execution	4) Used to store software called BIOS
5) can be written many times	5) Written once during the time of manufacturing.
The two main types of RAM are static RAM and dynamic RAM.	The types of ROM include PROM, EPROM and EEPROM.

5.4 RAM (RANDOM ACCESS MEMORY)

Random Access Memory is a temporary storage medium in a computer. All data to be processed by the computer are transferred from a storage device or keyboard to RAM during data processing. Results obtained from executing any program are also stored in RAM. RAM is a volatile memory. Latest computers use RAM with a memory of more than 128MB. There are provisions also available to increase the RAM memory in any computer.

RAM consists of many storage cells each of size 1 byte and is identified by using a number called as address or memory location. The memory address is assigned by the computer which also varies from computer to computer and time to time. The data stored in memory are identified using the memory address.

The internal processing speed of a computer is very fast compared to the reading and writing from/to disk. During the time of reading from disk the CPU is idle. To reduce this waiting time and increase the processing speed, a cache memory is used in the computer Cache memory is a part of RAM that holds the data, which is needed next by the CPU. The size of cache memory is 512 KB. Normally cache memory holds the recent information that is accessed. The data retrieval time for the processor from cache is more than the thousand times faster from disk., so the processing speed of a computer is improved.

There are two types of Random Access Memory (RAM). SRAM (Static RAM) and DRAM (Dynamic RAM) both holds data but in different ways. DRAM requires the data to be refreshed periodically in order to retain the data.

SRAM does not need to be refreshed as the transistors inside would continue to hold the data as long as the power supply is not cut off. This behavior leads to a few advantages, not the least of which is the much faster speed that data can be written and read.

Difference between SRAM and DRAM:

SRAM	DRAM
SRAM is static	DRAM is dynamic
SRAM is faster	Slower then SRAM
SRAM consumes less power	Consume more power
SRAM uses more transistors per bit	Uses less transistor per bit
SRAM is more expensive	Less expensive
Cheaper SRAM is used in main memory	DRAM is commonly used in cache memory

Double data rate synchronous dynamic random-access memory (DDR SDRAM):DDR RAM is the most frequently used RAM module in today's computer systems. There are different types of DDR RAM launch. First type is DDR1 RAM, also known as simply DDR RAM, has 184 pins that fit into the slot intended for it inside your computer on your motherboard.

Second type of DDR RAM is DDR2 RAM has 240 pins, and a notch at the bottom that is in a different location than the notch on DDR RAM. Thirdly latest version of DDR RAM is double data rate type three synchronous dynamic random access memory (DDR3), is a modern kind of dynamic random access memory (DRAM) with a high bandwidth interface. They are an improvement over DDR and DDR2 memory technology and deliver higher clock frequencies, lower power consumption and as a result lower heat dissipation.

5.5 ROM (READ ONLY MEMORY)

Read Only Memory is a permanent storage medium which stores start up programs. These programs which are loaded when computer is switched on. ROM stores essentially the BIOS (Basic Input Output System) programs which are recorded by the manufacturer of the computer system. ROM is non-volatile memory.

ROM is also known as firmware. In ROM programs are burnt during manufacturing. Normally system programs and language translators are stored in ROM chips.

Both ROM and RAM are semiconductor chips. Normally size of the ROM holds 8k and more depending on the requirement.

5.6 SECONDARY STORAGE

5.6.1 Floppy disk:

A floppy disk is used to store data permanently. It has a flexible disk coated with magnetic material and is enclosed in a plastic cover. Floppy disks are of 3 ½ inch diameter have a storage capacity of 1.44MB. The FDD (floppy disk drive) has a read/write head which reads/writes data on to the disk. The disk rotates at 360rpm while reading or writing on to it. Figure 3.1 shows the floppy disk.

Figure 5.2. A floppy disk

Data are stored in a floppy disk in concentric circles known as tracks. Tracks are divided into many storage locations called sectors. Tracks and sectors on a disk are identified by the disk

drive through formatting. Formatting is a process by which the operating system program controls the disk drives by removing the old data and sets up each track and sector. The root directory will be created in the disk during formatting and the users create other directories. Information is stored in the form of files. A file allocation table (FAT) is used by the operating system to identify the files stored in the disk.

5.6.2 Hard disk:

Hard disk is a reliable and permanent storage disk. It has a set of metal disks coated with magnetic material and are mounted on a central spindle which rotates at 7200 rpm. The HDD has a set of read/write heads which are mounted on an arm. Latest hard disks are available with a storage capacity of more than 40GB. Figure 3.2 shows a hard disk.

A hard disk has a collection of several (say 6 or 7) hard disk platters stacked one above another to have a high storage capacity.A collection of tracks across all the disks is called cylinder. In order to read a specified file, the access mechanism with the head moves to the specified cylinder.

The advantages of a hard disk are high storage capacity, high speed of operation and reliable media mainly in personal computers. External disturbances to the drive may lead to the damage of disk surface or read/write head. This is a major disadvantage in a hard disk.



Figure 5.3. (a) hard disk (b) Blu-ray Disc (BD) (c) shows CD-ROM

5.6.3 CD ROM:

Compact Disk (CD) is an optical disk used to store data permanently. It is the most reliable storage media available today. Data stored on a compact disk cannot be erased. The CD drives commonly available are read only. Read/Write CD drives are also available but are expensive. Storage capacity of CD is 700MB. Figure 3.3 shows a CD-ROM.

In the optical disk, a high power laser beam is used to record data by burning tiny pits in the surface of the hard plastic disk. To read the data, a low power laser beam is used to scan the disk surface. When the laser beam reflects from the smooth surface of the disk it is interpreted as a 1 bit and when the beam enters the tiny pits it is interpreted as a 0 bit.

The major advantages of the optical disk are high storage capacity and high quality recording of graphical images and sound. These are used commonly nowadays. CAD and structural drawings used by architects and engineers are generally stored in compact disks. It is also used in high quality music recording, multimedia and educational applications.

5.6.4 BLU-RAY

Blu-ray Disc (**BD**) Physically similar to CDs and DVDs, **blu-ray discs** are a huge leap forward, in terms of their storage format and memory capacity. Mainly used for the storage of high-definition video and data. The plastic disc is 120 mm in diameter and 1.2 mm thick, the same size as DVDs and CDs. Use of a blue laser to read and write data to a disc. The wavelength of a blue laser is substantially lesser that of the red laser used by the DVD format. A single-layer blu-ray disc can store 25 GB data, while a two-layer blu-ray disc is able to store 50 GB data. Triple layer discs (100 GB) and quadruple layers (128 GB) are available for *BD-XL* re-writer drives.

QUESTIONS

1. RAM is a --------memory.
2. Floppy 3 ½ disk storage capacity is -----.
3. Concentric circles in a floppy disk is known as -----
4. ROM is also known as -----.
5. ROM is a ----- memory.
6. Capacity of Hard disk is ---- than primary memory.
7. CD-ROM storage capacity is ---- .
8. Information stored in a cd is accessed through ----

Answers
1. Volatile
2. 1.44 MB
3. tracks
4. firmware
5. Nonvolatile
6. Bigger
7. 700 MB
8. laser beam

EXERCISES

1. Mention the storage devices used in a personal computer?
2. Explain primary memory its properties and its types?
3. What is the need for secondary storage? Briefly describe secondary storage devices like (i) Floppy disk (ii) hard disk (iii) CD ROM
4. Mention the components of a personal computer?
5. What is the difference between volatile memory and non-volatile memory?

CHAPTER 6

OPERATING SYSTEMS, APPLICATIONS, MULTIMEDIA AND NETWORKING

6.1 INTRODUCTION

We know software is a set of instructions that are used to carry out a task. Software can be grouped into two categories namely application software and system software. The application software is one, which is application oriented, like our inventory program, payroll program are few. Similarly system software is used for system oriented tasks. Examples are compilers, assemblers, loaders. In this chapter, we discuss the computer language fundamentals, application software and system software.

The objective of this chapter is to understand-
-Concept of machine, assembly and high level language.
-Role of compilers, assembler and interpreters.
-Difference between editor and word processor.
-Distinguish between application software and system software.
-Operating system functions.
-Features of DOS and UNIX.

6.2 COMPUTER LANGUAGES:

6.2.1 Machine language:

At the lowest level computer understands only 0 and 1. Programs expressed in terms of binary language are called machine language. A computer's programming language consists of strings of binary numbers (0's and 1's) and is the only one language computer can understand. This language is the lowest level of computer language recognized and used by the CPU. An instruction prepared in any machine language consists of 2 parts. The first part is the command or opcode or operation code. The second part of the instruction is the operand/s or data and it tells the processor where to find or store the data or other instructions that are manipulated. A short sample of machine language to perform addition in the storage location 0166 will look like this

00010000 00000001 01100010

A machine language programmer has to know the binary code for each operation to be carried out. Machine language programmers must also be familiar with the internal organization of the computer. A machine language programmer must also keep track of all the addresser of main memory locations that are referred to in the program. The machine language format is slow and tedious. We the human beings work on natural language and not on binary language. Hence writing machine language program is difficult for the humans.

6.2.2 Assembly language and Assembler:

A low level first generation computer language, popular during early 1960s, which uses abbreviations or mnemonic codes (mnemonic means mind full) for operation codes and symbolic addresses. This symbolic instruction language is called Assembly language. One of the first step in improving the program preparation was to substitute mnemonics for operation codes. The mnemonics are different among makes and models of computer. Second step was symbolic

addressing to express an address in terms of symbols convenient to the programmer. Another improvement was the programmer turned the work of assigning and keeping track of instruction addresses over to the computer. The programmer merely told the machine the storage address number of the first program instruction and the assembly language software the automatically stored all others in the sequence from that point.

The mnemonics are converted into binaries with the help of a translator known as Assembler.

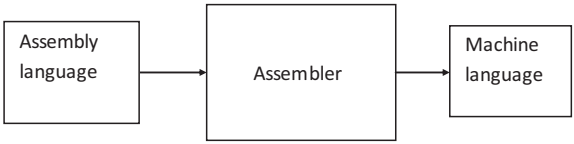


Figure 6.1: Function of an Assembler

The program written using mnemonics is called Source program or assembly language program , the binary form of the source program equivalent is called Object Program.Let us consider an assembly language program

```
LDA 9000
MOV B,A
MOV C,A
HLT
```

Assembler is used to convert assembly language into the machine language.
For example object program or machine language equivalent for the above assembly language is

```
01110 0100001100
01110011101
 0111110000
 1011100000
```


Assembly language programs are commonly used to write programs for electronic controls using microprocessors e.g., compilers , operating systems, animation in computer graphics and so on.

Assembly language is relatively easy for the human beings compared to machine language. Programs writing are faster compared to machine language.

Assembly language programmer should know details of the architecture of the machine. Assembly language programs are not portable.

6.2.3 Higher level languages and compiler:

Instructions which are written using English language with symbols and digits are called high level languages. The high level language is closer to our natural language. The commonly used high level languages are FORTRAN, BASIC, COBOL, PASCAL, PROLOG, C, C++ etc. The complete instruction set written in one of these languages is called a high level language program or computer program or source program.

In order to execute the instructions, the source program is translated into binary form by a compiler or interpreter. A compiler is also used to translate source program into an object

program. An interpreter is a program which takes the source program line by line and converts into machine code line by line.

C language uses a compiler as its translator to translate or compile the complete C program. It is also necessary to create an executable program to execute the instructions given in a source program by linking the input and output devices with your program. A linker (another program) is used to link library routing and generate an executable program from an object program. Compiler converts source program into object program in terms of stages called passes. Normally, most of the compilers uses two passes to convert source program into the machine language program.

Gwbasic is an interpreter used to convert basic program into object program.

6.3 COMPILER:

Compilers convert the program instructions from human understandable form to the machine understandable form and the translated program instruction is called object code. Compiler is nothing but a language translator used to translate the entire program of the high level language into machine language. Every programming language requires its own compiler to translate the program. For example, the programming language PASCAL requires PASCAL compiler and C uses C compiler.

Figure 6.2 Function of a Compiler

6.4 INTERPRETER:

Interpreters also convert the source program to machine language instruction but executes each line as it is entered. The translation of the source program takes place for every run and is slower than the compiled code. An interpreter must accompany the object code to run a program. Programming languages BASIC and LISP use interpreters.

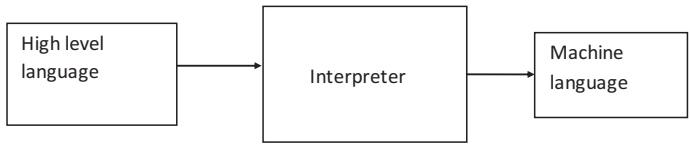


Figure 6.3 Function of Interpreter

6.5 EDITOR:

An editor is used to type the source program and store program in disk. C language uses one popular Boroland's a IDE (Integrated Development Environment) editor in MS-DOS system and in Vi editor in UNIX system. In dos, we use popular Edit editor also.

Editors are commonly used to type and edit documents and store them. Thus, they are also called text editors. In word processors we can perform the operation like setting up margins, spell check and so on. MS-WORD is one of the popular word processor.

6.6 SYSTEM SOFTWARE:

System software is designed for a specific type of hardware. For example, the disk operating system (DOS) is used to co-ordinate the peripherals of a computer. The system software controls the activities of a computer, application programs, flow of data in and out of memory and disk storage. Our operating system, compilers, assemblers, linker and loaders are the example of system software.

System software also handles data in communication applications and within the computer systems in a computer network. The communication software transfers data from one computer to another. These programs also provide data security and error checking along with the transfer of data between the computer systems.

6.7 APPLICATION SOFTWARE:

Application software are developed for application of the computer to common problems and tasks. They are available for business applications, science and engineering applications and so on. Personal productivity programs are categorized based on the nature of their use in word processing, generating spreadsheet, presenting graphics and maintaining databases. Application software is also available as packages and usually with a user manual.

Some of the application software are:

a) **Word processors**:

A word processor is used to prepare a report, a personal or business letter, in desktop publishing and so on. These offer formatting features such as using different character styles, line spacing, and page numbering and so on. Documents prepared using a word processor can be easily printed in any type of printer.

b) Electronic spread sheets:

An electronic spreadsheet software is used to prepare documents containing information or data in the form of numbers or characters. The information is arranged in rows and columns for further processing and analysis, preparing reports and generating charts. It is also capable of performing arithmetic operations and using functions.

c) Database software :

Databases are records related to a person or an organization. Database software have capability to edit and update data in a file. The data are processed to prepare and print salary details of employees, annual sales details and so on. One of the major applications of a computer is database management.

6.8 OPERATING SYSTEMS AND ITS FUNCTIONS:

We know operating system is a collection of programs and it is the interface between user and the computer. An operating system is a program which connects the user and the electronic hardware in a computer. It is a set of programs which supervise the activities of a computer and

activate the operations of the hardware components such as CPU, main memory, disk drives, keyboard, monitor and printer and so on. Some of the startup programs initially loaded to RAM are stored in ROM, mainly the BIOS programs which are recorded by the manufacturers of the computer system. Service programs available in operating system for operating system for operations like copying a file, deleting a file, formatting a disk, printing a file and so on are usually stored in the disk. Error messages are displayed on the screen if there is any malfunctioning of hardware.

There are many operating system used in computers. Commonly used operating systems are MS-DOS (Microsoft Disk operating System), Windows 95/98/2000, Windows NT, UNIX and so on. Nowadays Windows 2000 operating system is widely used in personal computers, and UNIX is used in Mainframes, Servers, Graphic Workstations and also personal computers. Linux is one of the most popular free operating system.

- Operating system will display instruction on the monitor screen and the user can interact with the computer.
- It loads the application programs such as MS Word ,AutoCAD and so on from disk to the computer memory.
- It manages the information stored on disk and retrieves the same whenever required.
- It supervises and coordinates the activities of the hardware and peripherals such as CPU, keyboard, mouse, monitor, printer, RAM, disk drives and so on.
- It utilizes the power of the CPU for multitasking and timesharing.

In general operating systems performs many task which include
Memory management
Process management
I/o management
Device management

6.9 MULTITASKING:

It is the ability of the computer to handle several application programs concurrently. Printing a document, executing a program and any other operation can be done simultaneously to reduce the idle time of the processor. The multi task capability of the operating system will utilize the processor efficiently, the reducing the user time. Another simple example is hearing audio songs and typing programs same time.

6.10 TIMESHARING:

It is the ability of the CPU to serve many users connected to it through a network. The operating system will assign each user a slice of processor time or time quantum in a round-robin fashion. Since the CPU has high processing speed, it can process information of many users.

6.11 SPECIFIC FEATURES OF DOS AND UNIX:

MS-DOS is a single user operating system developed by Microsoft Corporation. An operating system has a collection of program. When the computer is switched on, the file COMMAND.COM is loaded to the RAM and after the successful start of the computer, the DOS prompt or command prompt will be displayed. The DOS prompt displays the letter associated with the disk drive followed by a > symbol. For floppy disk drive , A> or A:> is displayed and for hard disk drive C> or C:\> is displayed. It indicates the operating system is ready to take commands from the user. MS-DOS is one of the popular operating system for desktop computers. DOS operating system consists of three parts in it, namely resident part, initialization

and the transient part. Most of the command programs are located in the resident part. While booting, the number of files and buffers to opened are contained in the initialization part and transient part is flexible part of the operating system. The commands are not case sensitive.

File:

A file is a collection of related information. For example , like the contents of a file folder in a desk drawer. Files on the disk can contain letters, memos and executable programs.

Program:

Programs are special types of files. These are series of instructions written in computer languages. These programs instructs the computer to perform the task.

Directory:

DOS uses a filing system to store its files. The filing system uses storage areas called directories. A directory is nothing more than an expandable file folder that can hold other expandable file folders. These file folders hold the data files. A directory is a table of contents for a disk. It contains the names of files, their sizes, and the dates they were last modified. All of the different directories are stored under one master directory. This directory is called the root directory.

In addition to directories, it uses an area on a disk called the File Allocation Table (FAT). The FAT is similar to our contents page in our book. It holds the information where the file is stored in the disk.

Multilevel directories:

When there are two or more users who share a computer, when you are working on several different projects, the number of files in the directory can become a large and unwieldy. Using directories is one way that we can divide our files into convenient groups. Any one directory can contain many files. This directory may also contain other directories or sub directories. This organized file structure is called a hierarchical directory system.

Specific features of UNIX:

The commands in UNIX are considered to case sensitive. It means, lower case a and uppercase A are considered differently.

Multitasking:

It refers to performing a number of tasks simultaneously. For example when a document is printed, you may run another program to sort large data and at the same time you may edit a document in the foreground screen. UNIX switches between the tasks and executes them one by one at small interval of time. This process of sharing the CPU to perform various tasks simultaneously is called time-sharing. The more number of the tasks are submitted then we end up with slower response from the computer.

Multi-user capability:

UNIX allows the computer to be used by several users through several terminal connected to a powerful computer. A terminal will have a keyboard and a monitor. The computer to which terminals are connected is called as the host computer or server. Any user on the terminal can run various programs, read file information or print a document at the same time. Multi user computer, are economical and efficient compared to stand-alone computers.

Portability:

One of the outstanding features of UNIX is its ability to port itself to another installation. For example, an application program developed in UNIX environment can be used in a different platform.

Security:

Unix provides a good security for users. The users are required to authenticate before they use the system. The password is encrypted.

File system

Unix identifies three types of users , owner, group and others. For each group it provides permission on the files like to read, write and execute operation.

6.12 PRELIMINARY COMMANDS OF DOS:

DIR command:

DIR command is an internal command which is used to display the contents in disk directory. To locate data files and programs on a specific disk, DOS uses the directory along with a file allocation table(FAT).

C:\>DIR

This command will display the disk directory in the default drive.

C:\>DIR/W

This command will display the disk directory in the default drive in a wide format.

C:\>DIR/P

This command will display the disk directory in the default drive but page wise. This command is useful when the disk contains numerous files.

C:\>DIR A:

This command will display the disk contents in A drive.

C:\>DIR *.C

This command will display the disk contents in the default drive with only the files having the extension .C. Here * is known as wild card character. It means all matching characters are represented by *.

CLS command:

CLS command is used to clear the screen. When this command is entered, all the previously displayed text or messages are removed from the screen. The syntax is:

C:\>CLS

REN or RENAME command

REN or RENAME command is used to rename an existing file. Consider the following example to rename a file in the current directory.

C:\>REN A.BAK A.C

Or

C:\>RENAME A.BAK A.C

When this command is entered, the file A.BAK is renamed as A.C.

DEL command

DEL command is used to delete files in a directory. Consider the following example to delete files in the current directory.

C:\>DEL A.BAK

This command will delete all the files in the directory . The message “Bad command or file name” is displayed when the file is not as available in the directory.

C:\>DEL *.BAK

This command will delete all the files in the directory with the extension .BAK The message “Bad command or file name” is displayed when the file is not as available in the directory.

C:\>DEL *.*

This command will delete all the files in the directory. When this command used,the message “Are you sure to delete all files(y/n)?” is displayed. Press y to confirm deletion.

ERASE command

ERASE command is used to erase or remove files in the directory. Consider the following examples to erase files in the directory.

C:\> ERASE A.BAK

This command will erase the file A.BAK in the directory. The message “Bad command or file name” is displayed when the file is not as available in the directory.

C:>\ ERASE *.*

This command will erase all the files in the directory. when this command is entered, the message “Are you sure to delete all files(y/n)?”, is displayed. Press y to confirm deletion.

DATE command

DATE command is used to display the current system date. The computer also maintains a calendar. This command will display the current system date in mm-dd-yy(month-date-year) format and the user may enter the new date. Consider the following example to display the current date.

C:\>DATE

Current date is Sun 09-25-2005

Enter new date (mm-dd-yy):

TIME command

TIME command is used to display the current system time. The computer also maintains a clock. This command will display the current system time in (hours:minutes: seconds) format and the user enter the new time. Consider the following example to display the current time.

C:\> TIME

Current time is 11:37:25.34p

Enter new time:

CD command

CD(change Directory) command is used to change the directory to another specified directory/location in the disk. A message “Invalid directory” is displayed if the directory mentioned is not available. Consider the following example

(i) C:\>CD ABC

This command will change the current directory to the specified directory ABC in the disk. Now the prompt is displayed as follows.

(ii) C:\>CD FC

C:\TC>CD ABCP

These commands will change the current directory to the specified directory TC and then to the directory ABCP in the disk. Now the prompt is displayed as follows.

C:\TC\ABCP>

C:\>CD\TC\ABCP

This command will also change the directory to the specified directory TC and then to the directory ABCP in the disk. Now the prompt is displayed as follows.

C:\TC\ABCP>

CD command can be used in the following ways to quit from a directory or transfer the control to a root directory

C:\TC\ABCP>CD\

C:\TC>CD..

C:\>

MD command

MD(Make directory) command is used to create a new directory in the storage device to store programs. Consider the following example to create a new directory:

C:\>MD ABCP

This command will create a new directory in the current directory. To transfer the control to the new directory a CD command is used.

C:\>CD ABCP

CD:\ABCP>

RD Command

RD(Remove Directory) command is used to remove a directory permanently from the disk. Note that all the files in that directory should be removed before the RD command is used. Also know that you should quit from the directory being removed. Consider the following example:

C:\TC RD ABCP

C:\TC\ABCP>DEL *.*

All files in directory will be deleted!

Are you sure(y/n)? Press y to confirm the delete option.

C:\TC\ABCP>CD..

C:\TC>RD ABCP

One of these commands can be used to remove the directory ABCP from the disk.

COPY command

COPY command is used to copy a file to a new location or directory in the disk. A file cannot be copied to itself in the same directory in the same name.

Consider the following example:

C:\>COPY AB.TXT AB.BAK

This command will copy the file AB.TXT in the same directory as AB.BAK. The first file name in the command AB.TXT is the source file and the file AB.BAK is the target file which is a copy of AB.TXT.

C:\>COPY AB.TXT A:

This command will copy the file AB.TXT from the C drive to A drive and is copied in the same name.

C:\>COPY AB.TXT A: AB.BAK

This command will copy the file AB.TXT from the C: drive to A: drive but the target file is named as AB.BAK.

C:\>COPY *.* A:

This command will copy all the files in the current directory of C: drive to A: drive in the respective file names

C:\>COPY *.* A:

This command will copy all the C program files in the current directory of C: drive to A: drive in the respective file names.

The COPY command can also be used to create a file in the console using the keyword CON along with COPY command.

C:\>COPY CON sample.txt

TYPE command

This command is used to display the contents of a file on the monitor screen. Consider the following example

C:\>TYPE AB.TXT

This command will display the contents of the file AB.TXT on the screen. TYPE command can also be used to send the contents of the file to the printer in the console using the keyword PRN.

Consider the following example

C:\>TYPE AB.TXT >PRN

This command will print the contents of the file AB.TXT

FORMAT command:

FORMAT command is used to format a new disk. It is an utility program that is available on hard disk. Only the formatted disks can be used by the operating system to store files or programs. Consider the following example to format a new floppy disk. Insert the new floppy disk in A drive and give the following command.

C:\>FORMAT A:

Nowadays new formatted floppies are available in packs which need not be formatted again. If any old floppy is formatted then the contents will be erased automatically.

DISKCOPY Command:

DISKCOPY command is used to copy all the contents of various directories of a disk in another disk. It is faster and useful to take backup copies.

Consider the following example:

C:\>DISKCOPY A: C:

Now the contents of floppy disk in A drive is copied to the hard disk drive C.

CHKDSK command:

CHKDSK command is used to get the report about a disk such as disk directories,files, storage space available etc. Consider the following example to check the floppy disk in drive A

C:\>CHKDSK A:

Now the details of floppy disk in A drive is displayed. It is also possible to display details using the SCANDISK command.

6.13 UNIX COMMANDS:

Who command :

Who command is used to list users who are currently logged to the system. The username together with the terminal, date and time the user last logged will be displayed.

```
$who
abhi  tty1  sep 29 13:01
reva   tty2  sep 29  14:15
user1  tty3  sep 29  15:45
$
```

$who –u

This option –u(means unused) will list the user with the unused time shown below

```
$who
abhi  tty1  sep 29 13:01  00:05
reva   tty2  sep 29  14:15  01:20
user1  tty3  sep 29  15:45
$
```

Note that the users abhi and reva were idle for 5 minutes and 1 hour 20 minutes respectively.

To display user name, terminal line, date and time of login, the who command is given as follows.

```
$who am i
user1 tty3 sep 29 15:45
```

to confirm login name, type the following command

```
$ logname
user1
$
```


pwd Command:

pwd(print working directory) command will display the current working directory.

```
$pwd
/usr/user1
$
```

Note that /(slash) represents the root directory. In MS DOS, the root directory is represented by \(back slash)

echo command:

echo command will display the text typed from the keyword. Consider the following example

```
$ echo Learning UNIX is fun
Learning UNIX is fun
$
```

cat command

cat command is the simplest way to create a file. It is equivalent to the copy con command in MS DOS. It takes names of zero or more files as argument. Consider the following example.
With no arguments ,cat will take input from the keyboard.

```
$ cat
welcome
welcome
-have a nice day
have a nice day
ctrl –d
$
```

note that the cat command echoes each line as soon as it has been typed in.

sort command:

sort command is used to sort the contents of a file and name it students_list

```
$cat > students_list
Abhi        20101
Revathi     20125
Preethi     20104
Ravi        20121
ctrl –d
$
```

using sort command, the above list may be sorted alphabetically as shown below

```
$sort students_list
Abhi      20101
Preethi   20104
ravi      20121
Revathi   20125
```


wc command

wc command is used to count the number of lines, words and characters in a file. Consider the following example.

```
$wc students_list
5 10 53 students_list
```

note that there are 5 lines,10 words and 53 characters in the file. Also note that every line is terminated by pressing Enter key which is represented by an invisible new line character. These characters are also accounted to get the number of characters as 53 instead of the actual number of characters as 48.

The wc command has the following options

(i) $ wc –l will display the number of lines in a file.

Example:

```
$wc -l  students_list
 5 students_list
```

(ii) $ wc –w will display the number of words in a file.

```
$wc –w students_list
10 students_list
```

(iii) $ wc –c will display the number of characters in a file.

```
$wc –c students_list
  53  students_list
```

grep command:

grep command is used to search and display a line for a given word or pattern in a given file name. consider the following example to display the register number of a student.

```
$grep Abhi students_list
  Abhi  20101
```

Filters:

These refer to any command that can take input from standard input, perform some operations and write the results to standard output.
Consider the following example:

```
$ who
cseabhi  tty1  sep 29 13:01
itreva   tty2  sep 29  14:15
ituser1  tty3  sep 29  15:45
$
```

The above list can be short listed to specific users and display the list in alphabetical order as shown below.

```
$ who | grep it | sort
itreva   tty2  sep 29  14:15
ituser1  tty3  sep 29  15:45
$
```

The output of who is fed into the input of grep which will filter and display those users containing the pattern it.

ls command:

ls command is used to list the files stored in the directory
consider the following example

```
$ls
jp.c    test1    sample1     sample2
sam.txt   ex1.c   letter.doc
```

the following options are available with ls command.
The ls –l option is used for long listing of files in the current directory.

```
$ls -l
total 24
dwxr-xr-x2    user1  group   480   Sep 05  02:15   first.dir
-rw-r—r--  1  abhi     group     80  Sep 05 02:13  myfile.c
-rw-r—r--  1  reva   group     80   Sep 05  02:34    jp.c
```

$ls –r will display files in reverse alphabetically order.
$ls* will display all the files and directories in the current directory.

$ls* will display all the files and directories in the current directory.

mkdir command:

mkdir command is used to create a new directory . Consider the following example

```
$mkdir jpdir
$
```

will create a directory named jpdir

rmdir command:

rmdir command is used to remove a directory. Consider the following example.

$rmdir jpdir
$
note that all fields in the directory should be deleted before removing that directory.

cd command:

cd command is used to switch from the current directory to another directory. Consider the following example.
$ cd tjp
$
note that the current directory will now be tjp. The following options are available with cd command.
$cd or $cd .. is used to switch to the home directory.

$cd/usr/user1 is used to switch to the directory user1.

cp command:

cp command is used to copy a file. Consider the following example.
$ cp jp.prg jp.copy
$
note that jp.prg is an existing file which will be copied as jp.copy. if the file jp.copy already exists in the same directory,it will be over written without any warning.
The following options are available with cp command.
$cp jp.prg/usr/usr1 is used to copy the file to the specified directory.
$cp jp.prg/usr/user1/jp.bak is used to copy and change the name of the file.

rm command:

rm command is used to remove or delete a file. Consider the following example
$rm jp.bak
$
the file jp.bak will be permanently removed without any warning.
The following options are available with rm command
$rm –i jp.bak will remove a file after confirmation from the user.
Rm: remove 'jp.bak' ? y press y then enter to delete the file.
$

mv command

mv command is used to rename a file. Consider the following example.
$mv jp jp.c
$
note that the file jp is renamed as jp.c

man command

man command is used to display the help manual for UNIX commands.

QUESTIONS

1. Machine language is expressed in terms of -----.
2. Assembly language is written with the help of ------
3. High level language is similar to -------
4. Compiler converts ---- language into ---- language.
5. Assembler converts ----- language into ---- language.
6. Interpreter converts high level language into machine language ---- by ----.
7. edit is an example of ------.
8. Ms-word is an example of ------
9. To display files in the MS-DOS , ---- command is used.
10. To display copy a file in Unix --- command is used.
11. In Unix , commands are ---- sensitive.

Answers

1. 0 and 1.
2. Mnemonics
3. English
4. High, machine
5. Assembly , machine
6. line , line
7. editor
8. word processor
9. DIR
10. cp
11. case

EXERCISES

1.What is a machine language?

2. Explain assembly language and an assembler?

3. Mention any three higher level languages?

4. What is a compiler?

5. Give the differences between compiler and interpreter?

6. What is a source program?

7 . List the functions of an editor?

8. Differentiate between system software and application software?

9. Explain operating system and its functions?

10. Write the specific features of DOS and UNIX operating systems?

11. Explain any five MS-DOS commands and UNIX commands ?

6.14 COMPUTING ENVIRONMENTS:

6.14.1 INTRODUCTION:

We know, in information technology era, sharing of resources and easy communication are acting as a backbone of any network. Popular example is our Internet. With the help of internet we are able to exchange information and share resources. Hence in this chapter we study different advantages of the network and different forms of the network and their features.

The learning objectives of this section are to know
-What is a computer network ?
- How network is advantageous ?
-What are different forms of networks ?
-What is a e-mail ?

6.14.2 NETWORKING OF COMPUTERS AND ITS ADVANTAGES.

Computer network is defined as an interconnection of autonomous computer. Here autonomous means, there is no master and slave relationship. All computers are equal. Computer network enables to share the resources. Computer networking also refers to connecting computers to share data, application software and hardware devices. Networks allow sharing of information among various computers and permit users to share files. For example a students accesses compilers sitting at one place, where compiler may be stored on the other machine. The students takes printout with the help of one printer connected to the network. The printer can be shared among many students.

Network offers the opportunity to communicate more efficiently with others through electronic mail. Networks allow companies to share software and peripherals such as printers, plotters, scanners and so on. With networking all the computers in an office can be connected to a single printer and scanner. It also helps in using storage devices efficiently.

Computer network acts as a very powerful communication medium. It means people exchange their information. When compared to mainframe computers, network of computers saves money.

6.14.3 TYPES OF NETWORKS

Depending the nature of the distances, protocols (the set of rules used for communication) the network can be classified into LAN (Local Area Network), MAN (Metropolitan Area Network) and WAN (Wide Area Network).

6.14.3.1 Local Area Network (LAN)

A **LAN** (local area network) is a group of computers and network devices connected together, usually within the same building. By definition, the connections must be high-speed and relatively inexpensive (e.g., token ring or Ethernet). They function to link computers together and provide shared access to printers, file servers, and other services.

Any individual computer connected to a network is called workstation. A workstation may not need a floppy disk or hard disk. A LAN or local area network connects computers and peripherals in a limited area. LAN requires cables to connect workstations. For example LAN is used in a hall or within a building. Figure 6.1 shows Local Area Network , where various departments are connected.

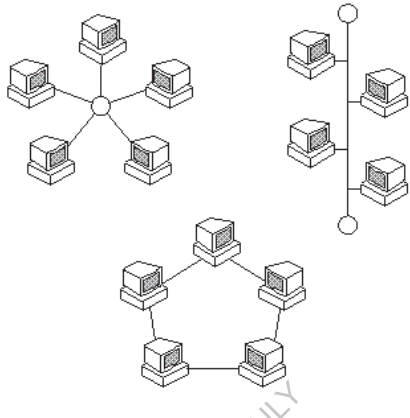


Figure 6.4. Local Area Networks

6.14.3.2 Metropolitan Area Network (MAN):

A MAN (Metropolitan Area Network) is used to connect computers to cover the city or town. The range may be approximately 50 Kilometers. Normally cables and fiber optic cables are used to connect computers. The routing of the messages are fast. Normally central library in a city may be connected by a MAN, so users can access the information. Figure 6.2 shows a typical view of Metropolitan Area Network.

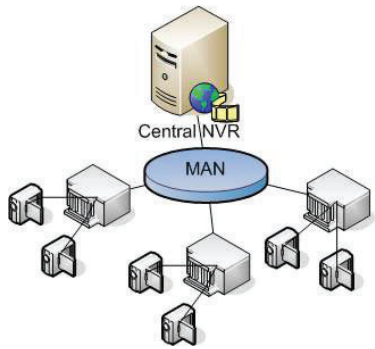


Figure 6.5. Metropolitan Area Network

6.14.3.3 Wide Area Network (WAN)

A WAN (Wide Area Network) covers large distance like state, country or continents. The WAN uses the fiber optics, cables and even satellites also. Here communication circuits are connected with the help of hardware device called routers. Routers forward small pieces of information called packets from one to another. Internet is the popular one comes under WAN. Some of the examples makes use of internet are reservation of airplane tickets, railway tickets and even cinema tickets. Another facility called e-commerce, where business is carried out through internet. Here people can buy books, articles and so on through registering their wants through the internet. Figure 6.3 shows a typical view of Wide Area Network.

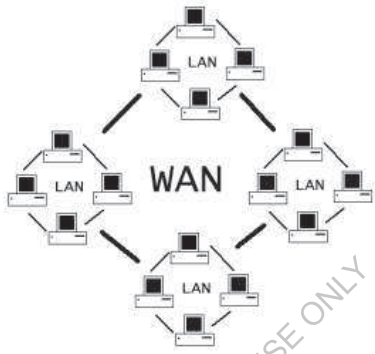


Figure 6.6. Wide Area Network

6.14.4 INTERNET:

The internet is a massive wide area network ,connecting thousands of computer networks around the world. The internet is a world wide "network of networks". It is a collection of thousands of smaller networks in different countries around the world. It links thousands of academic government, military and public computers, enabling millions of people to share information and other resources.

Internet pathways are used to exchange digitized computer data. The basic services that form the foundation of the internet are e-mail , telnet and FTP. With internet we can easily exchange electronic mail with friends and family anywhere in the world.Telnet allows you to connect to a remote computer. We can access any of the public services or tools and library databases at the remote site. FTP(File Transfer Protocol) provides for transferring files from one computer to another across the internet.Internet has many uses. For individuals, the most important uses of internet are e-mail and surfing the Web. One can read the topics of interest like sports, a hobby, a country or any place of interest.

E-mail:

The e-mail stands for electronic mail. One of the major features of computer networking is that messages can be sent electronically to various terminals on the network. The messages are sent very quickly and accurately. E-mail uses the concept of Storing and forwarding messages. It saves a lot of money for the users. Here user registers his/her account with one of the providers. The e-mail account normally contains username and the provider name. For example abc @ yahoo.com , represents abc is the name of the user , who is registered in yahoo provider.

QUESTIONS

1. Computer network defined as a interconnection of ---------- computers
2. Computer network allows user to ----- the resources
3. -------- network confined to hall or building.
4. ------- is one example of WAN.
5. ------ business is carried our through internet.
6. Small piece of information called ---- are forwarded by router in Internet.

ANSWERS

1. Autonomous
2. share
3. Local area
4. Internet
5. E-commerce
6. packets

EXERCISE

1. What is a computer network ? What are the advantages of computer network ?
2. Briefly explain the Local area network, Metropolitan area network and wide area network.
3. What e-mail ? How e-mail works ?
4. What are the uses of Internet ?

CHAPTER 7

PROGRAM DESIGN FUNDAMENTALS

7.1 ALGORITHMS AND FLOWCHARTS:

7.1.1 ALGORITHMS :

The fundamental knowledge necessary to solve problems using a computer is the notion of an algorithm. An algorithm is a precise specification of a sequence of instructions to be carried out in order to solve a given problem. Each instruction tells us what task is to be performed.

The example below will make you understand the specifications:

Example: Recipe for Mutter paneer
Ingredients:
½ kg fresh onion, 400 gms paneer, 2 onoins grated, 2 tomatoes, peeled and chopped 1tsp chilli powder, ½ cup coriander leaves,1/2 turmeric powder,1tsp garlic/ginger paste,4 tsp oil,salt to taste.

Method:
Step 1: Pressure cook onion in Pressure Pan with 1 ½ cups of water. Drain out excess water, keep onion aside.
Step 2: Heat oil in the pressure pan and add the onions. Saute' till they turn brown then add tomato pulp.
Step 3: Add spices, garlic and ginger paste, saute' till the gravy is well blended.
Step 4: Add cooked onion,paneer and salt.
Step 5: Simmer for 5 minutes.
Step 6: Garnish with coriander leaves.
Result: Mutter paneer ready to serve for 4 people.

The recipe given above is similar to an algorithm but it does not technically qualify as one as the instructions given above are not precise it depends on the individual whether the person has to wait for the gravy to be blended.

We will look at another example to examine another sequence of instructions:
Instructions to knit Sweater:

Input
Needles No.12=2
Wool 4 ply = 9 balls

Method
Step1 : Cast on 133 stitches
Step2: Repeat Steps 3 and 4, 11 times
Step3: Knit 2, *Purl 1, Knit 1, Repeat from * to last stitch, Knit 1.
Step 4: Knit, *Purl 1, Knit 1, Repeat from * to End
……
……
(Similar steps)
Result : A Sweater

The above example shows:
1. The instructions are much more precise and unambiguous when compared to the recipe for mutter paneer.
2. The number of different types of actions to be carried out are very few.
3. By a proper permutation and combination of this elementary set of actions a virtually infinite number of patterns may be created.

Computers are built to carry out a small variety of elementary instructions. A computer may thus be thought of as a servant who would carry out instructions at very high speed obediently and uncritically. There is a need to give the computer extensive, detailed and correct instructions for solving problems. In order to do this there is need for algorithms which have to be precise, concise and unambiguous.

7.1.2 FLOWCHARTS:

A flowchart depicts pictorially the sequence in which instructions are carried out in an algorithm. Flow charts are used not only as aids in developing algorithms but also to document algorithms.

For visual recognition a standard convention is used in drawing flowcharts. In this standard convention
(i) Parallelograms are used to represent input and output operations.
(ii) Rectangles are used to indicate any processing operation such as storage and arithmetic
(iii) Diamond shaped boxes are used to indicate questions asked or conditions tested based on whose answers appropriate exits are taken by a procedure.
(iv) Rectangles with rounded ends are used to indicate the beginning or end points of a procedure.
(v) A circle is used to join different parts of a flowchart. This is called a connector.
(vi) Arrows indicate the direction to be followed in a flowchart.

Example 7.1 Algorithm and flowchart for finding biggest of three numbers:

Finding the biggest of three numbers
Step1: Read three numbers A, B, C
Step2: Compare A with B
Step3: If A is larger compare it with C
Step4: If A is larger than C then A is the largest otherwise C is the largest.
Step5: If A is smaller than or equal to B in the first step then B is compared with C.
Step6: If B is larger than C then B is the largest number otherwise C is the largest number.
Step7: Stop

The above algorithm may be expressed much more clearly and concisely using a flowchart.

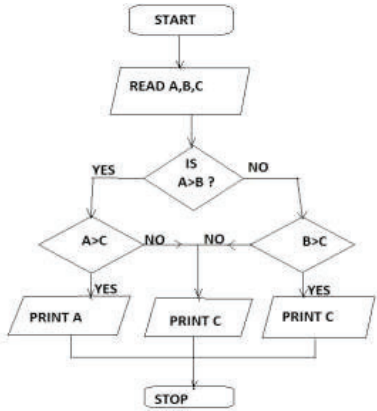


Figure 7.1. Flowchart depicting the largest of three numbers. - A

Example 7.2 Algorithm to count the number of non-zero data

Step1: Initialize the non-zero data counter nzdcount to 0
Step2: Repeat 100 times all steps up to Step4
Step3: Read d
Step4: If d is not equal to 0 then
nzdcount =nzdcount+1
Step5: Print nzdcount
Step6: Stop

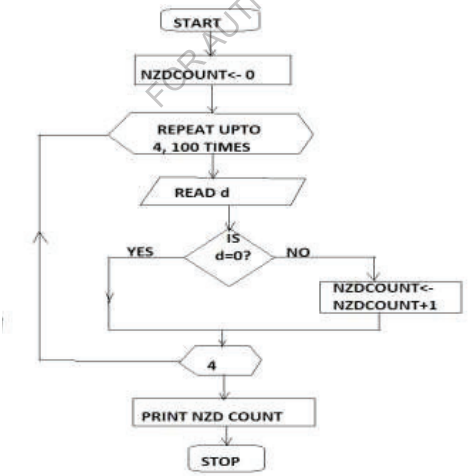


Figure 7.2 Flowchart depicting the number of non-zero data

Example 7.3 Algorithm to find the biggest and smallest of given set of numbers

Step1: Read Number
Step2: Assign the number to the value Largest
Assign the number to the value Smallest
Step3: Repeat steps 4 and 5 as long as numbers are there.
Step4: Read number
Step5: If the number is greater than largest then the number is largest.
If the number is lesser than smallest then the number is smallest.
Step6: Write Largest number
Write Smallest number
Step 7: Stop

Flowchart to depict the biggest and smallest of given set of numbers. –Left as exercise for reader.

Example 7.4 Algorithm to solve the given quadratic equation:

Step1: Read three numbers a, b, c
Step2: Multiply number b twice
Step3: Multiply number 4 with a and c
Step4: Subtract the result of step2 from the result of step3
Step5: Find the square root of the result obtained in Step4
Step6: Add the result of step5 with the negative of number b
Step7: Multiply the number 2 with a
Step 8: Divide the result of step 6 by the result of step 7
Step9: Similarly subtract the result of step5 with the negative of number b
Step10: The result is obtained for the quadratic equations for values x1 and x2.
Step11: Stop.

Flowchart depicting the solution for the quadratic equation. –Left as exercise for reader.

7.2 DATA FLOW DIAGRAMS (DFDS):

Data Flow Diagrams (DFDs) are a graphical/representation of systems and systems components. They show the functional relationships of the values computed by a system, including input values, output values, and internal data stores. It's a graph showing the flow of data values from their sources in objects through processes/functions that transform them to their destinations in other objects. Some authors use a DFD to show control information, others might not. A DFD can be seen as a method of organizing data from its raw state.

Steps for developing DFDs:

Step 1: Requirements determination
This is the result of the preceding phases. Through different techniques, the analyst has obtained all kinds of specifications in natural language. This phase never stops until the construction of the DFD is completed. This is also a recursive phase. At this moment, he should filter the information valuable for the construction of the data flow diagram.

Step 2: Divide activities
Hereby, the analyst should separate the different activities, their entities and their required data. The completeness per activity can be achieved by asking the informant the textual specification with the lacking components in the activity.

Step 3: Model separate activities
The activities have to be combined with the necessary entities and data stores into a model where input and output of an activity, as well the sequence of data flows can be distinguished. This phase should give a preliminary view of what data is wanted from and given to whom.

Step 4: Construct preliminary context diagram
The organization-level context diagram is very useful to identify the different entities. It gives a steady basis in entity distinction and name giving for the rest of the construction. From here on, the analyst can apply his top-down approach and start a structured decomposition. This is the process of organizing the diagrams into a hierarchy of increasingly detailed views of processes.

Step 5: Construct preliminary level 0 diagrams
The overview, or parent, data flow diagram shows only the main processes. It is the level 0 diagram. This diagram should give a 'readable' overview of the essential entities, activities and data flows. An overdetailed level 0 diagram should generalize appropriate processes into a single process.

Step 6: Deepen into preliminary level n diagrams
This step decomposes the level 0 diagrams. Each parent process is composed of more detailed processes, called child processes. The most detailed processes, which can not be subdivided any further, are known as functional primitives. Process specifications are written for each of the functional primitives in a process.

Step 7: Combine and adjust level 0-n diagrams
During the structured decomposition, the creation of the different processes and data flows most often generate an overlap in names, data stores and others. Within this phase, the analyst should attune the separate parent and child diagrams to each other into a standardized decomposition. The external sources and destinations for a parent should also be included for the child processes.

Step 8: Combine level 0 diagrams into a definitive diagram
The decomposition and adjustment of the levelled diagrams will most often affect the quantity and name giving of the entities.

Step 9: Completion
The final stage consists of forming a structured decomposition as a whole. The input and output shown should be consistent from one level to the next.

Example : Draw the DFD for an Educational Institution.

1. **Context diagram:**

It is the highest level DFD.It has data flows, external entities, one process (system in focus) and no data stores.Shows the system boundary and interactions with external entities.

In this case:
External entity - Student
Process - Student Administration process application
Data Flows - Application Form, Confirmation/Rejection Letter

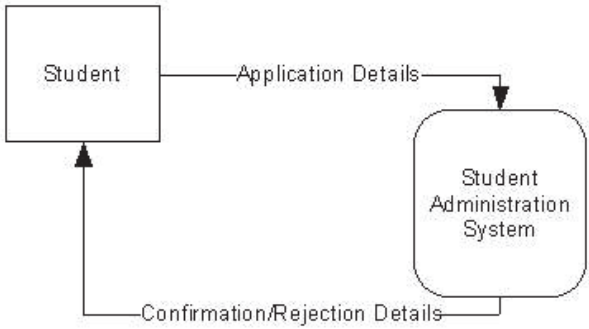


Figure 7.3. Context diagram

2. Level 0 DFD

External entity - Student
Processes - Check available, Enrol student, Confirm Registration
Data Flows - Application Form, Course Details, Course Enrolment Details, Student Details,Confirmation/Rejection Letter
Data Stores - Courses, Students.

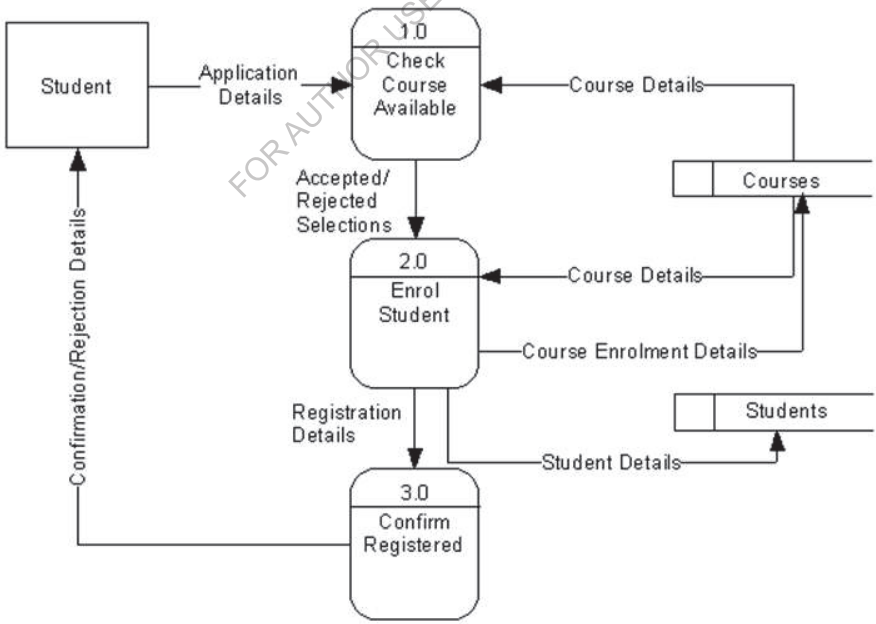


Figure 7.4. Level 0 DFD

EXERCISES

1. Discuss importance of algorithms and flowcharts in program design and development.
2. Write an algorithm for checking whether a number is prime or not. Draw the flowchart for the same.
3. What is DFD? Discuss its importance in software development.
4. Draw the flowchart for converting temperature from celcius to kelvin. Also write the reqired algorithm.
5. Write an algorithm to find simple interest.

CHAPTER 8

INTODUCTION TO C

8.1 WHAT IS C?

Digital computers operate in two voltage levels. The high one (commonly 5-4V) is represented by binary bit 1 and the low one (0-0.8V) represented by 0. To perform any task using a digital computer one must fed the computer a sequence of combinations of 1's and 0's (high and low voltages) corresponding to that specific task. This is called machine understandable or simply machine language. Very well trained people specific to the hardware of that particular machine are required to operate and perform any job using machine language. To make this a bit more understandable some specific sequence of bits are given special names using english alphabet. Any sequence of such names called mnemonics to accomplish a task is called an assembly language program.

Assembly language is also not too friendly to be used by anybody. It requires well experienced people to write programs in some well specified format specific to a computer hardware configuration and it does not provide too much flexibility to write more complex programs of today's age. So, there was an obvious need to design language that is friendlier to be used by common people and that provides more flexibility to write complex but easily understandable programs called a high level language.

A number of high level languages was developed earlier but Dennis Ritche while writing the UNIX operating system at AT&T Bell Labs. felt the necessity of a more flexible high level language for making his task more easier. In 1969 BCPL -- a user friendly OS providing powerful development tools developed from BCPL. A new language "B" was developed in a second attempt in 1970. Later a totally new language "C" a successor to "B" was developed in 1971.By 1973 UNIX OS almost totally written in "C".

8.2 CHARACTERISTICS OF C :

We briefly list some of C's characteristics that define the language and also have lead to its popularity as a programming language. Naturally we will be studying many of these aspects throughout the course.

- Small size
- Extensive use of function calls
- Loose typing -- unlike PASCAL
- Structured language
- Low level (Bitwise) programming readily available
- Pointer implementation - extensive use of pointers for memory, array, structures and functions.

C has now become a widely used professional language for various reasons.

- It has high-level constructs.
- It can handle low-level activities.
- It produces efficient programs.
- It can be compiled on a variety of computers.

Its main drawback is that it has poor error detection which can make it off putting to the beginner. However diligence in this matter can pay off handsomely since having learned the

rules of C we can break them. Not many languages allow this. This if done properly and carefully leads to the power of C programming.

8.3 C CHARACTER SET:

The character set of characters of C language consists of

- Alphabets A,B,C,……..Z,a,b,c,……..z,
- Digits 0,1,……..9,
- Special Symbols {} [] () + - / * ! ~ = : ? <> |‘’ “ ; , . @ # % ^ & * - \

8.4 C VARIABLES AND CONSTANTS:

Variables and constants are named memory elements; the value of a variable may change whereas that of a constant does not.
In C variable or constant name can be created using alphabets and the symbol ‘_’.
e.g., a variable int a;
a constant const int b=10; or #define b 10;

8.5 C KEYWORDS:

C language consists of 32 basic keywords which can not be used as variable names, listed below.

auto	Double	if	static
break	Else	int	struct
case	Enum	long	switch
char	Extern	near	typedef
const	Float	register	union
continue	Far	return	unsigned
default	For	short	void
do	Float	signed	while

8.6 C INSTRUCTIONS:

We can construct meaningful sentences called instructions in C language using variables,constants,special symbols and keywords.There are mainly four types of instructions in C.

1. Data type declaration instructions : used to declare the type of variable in the C program.
   e.g., `int a; float b; char c;`
2. Input /Output (I/O) instructions : used to feed data (input) to and get and get result (output) from a program.
   e.g., `scanf("%d",&a); printf("%d",a);`
3. Arithmatic instructions : used to perform arithmatic operation between constants and variables.
   e.g., `average=(a+b+c)/3;`
4. Control instructions : used to control sequence of execution of various statements in a C program.
   e.g., `do{ c=a+b;}while(a>5);`

8.7 C PROGRAM:

A set of meaningful instructions groped together in a specified order (sequence) to perform a spefied task may be called a program.

C Program Structure :

A C program basically has the following form:

- Preprocessor Commands
- Type definitions
- Function prototypes -- declare function types and variables passed to function.
- Variables
- Functions

We must have a main()function.

e.g., Job : Find sum of two integers taken as input from the keyboard and display it.

Program :

```
/* This program finds the sum of two integers taken as input
from the keyboard and displays it*/
   1. #include<stdio.h>
   2. main(){
   3. int a,b,c;
   4. printf("Enter the two numbers.\n");
   5. scanf("%d%d",&a,&b);
   6. c=a+b;
   7. printf("The Sum is  : %d",c);}
```

Result:

input : Enter the two numbers. 1 2

output : The Sum is : 3

Explanation :

`/* This program ... */` The symbols /* and */ delimit a comment. Comments are ignored by the compiler , and are used to provide useful information for *humans* that will read the program.

`#include<stdio.h>` is a preprocessor command

main() C programs consist of one or more functions. One and *only* one of these functions must be called main. The brackets following the word main indicate that it is a function and not a variable.

`{ }` braces surround the body of the function, which consists of one or more instructions (*statements)*.

`int a,b,c` are declaration of variables.

`;` terminates a statement.

printf() is a library function that is used to print on the standard output stream (usually the screen).

`"Enter the two numbers\n."` is a string constant.

`\n` is the newline character.

`scanf()` is a library function that is used to read from the standard input stream (usually the keyboard).

C is case sensitive, so the names of the functions (main and printf) must be typed in lower case as above.

8.8 EXECUTING (CREATING, COMPILING AND RUNNING) A C PROGRAM :

The stages of developing your C program are as follows.

Creating the program :

Create a file containing the complete program, such as the above example. You can use any ordinary editor with which you are familiar to create the file. One such editor is *textedit* available on most UNIX systems.

The filename must by convention end ``.c" (full stop, lower case c), *e.g. myprog.c* or *progtest.c*. The contents must obey C syntax. For example, they might be as in the above example, starting with the line `/* Sample ....` (or a blank line preceding it) and ending with the line `} /* end of program */` (or a blank line following it).

Compilation :

There are many C compilers around. The `cc` being the default Sun compiler. The GNU C compiler `gcc` is popular and available for many platforms. PC users may also be familiar with the Borland `bcc` compiler.

There are also equivalent C++ compilers which are usually denoted by `CC` (*note* upper case CC. For example Sun provides CC and GNU `GCC`. The GNU compiler is also denoted by `g++`

Other (less common) C/C++ compilers exist. All the above compilers operate in essentially the same manner and share many common command line options. However, the **best** source of each compiler is through the online manual pages of your system: *e.g.* `man cc`.
For the sake of compactness in the basic discussions of compiler operation we will simply refer to the `cc` compiler -- other compilers can simply be substituted in place of `cc` unless otherwise stated.

To Compile your program simply invoke the command `cc`. The command must be followed by the name of the (C) program you wish to compile.

Thus, the basic compilation command is:

```
cc program.c
```

where *program.c* is the name of the file.

If there are obvious errors in your program (such as mistypings, misspelling one of the key words or omitting a semi-colon), the compiler will detect and report them.

There may, of course, still be logical errors that the compiler cannot detect. You may be telling the computer to do the wrong operations.

When the compiler has successfully digested your program, the compiled version, or executable, is left in a file called *a.out* or if the compiler option *-o* is used : the file listed after the *-o*.

It is more convenient to use a *-o* and filename in the compilation as in

```
cc -o program program.c
```

which puts the compiled program into the file program (or any file you name following the "-o" argument) **instead** of putting it in the file a.out .

Running the program :

The next stage is to actually run your executable program. To run an executable in UNIX, you simply type the name of the file containing it, in this case *program* (or *a.out*)
This executes your program, printing any results to the screen. At this stage there may be run-time errors, such as division by zero, or it may become evident that the program has produced incorrect output.

If so, you must return to edit your program source, and recompile it, and run it again.

8.8.1 Steps to do to execute a C program under DOS Environment TurboC :

- **to start TurboC** type TC in DOS prompt or open TC\BIN directory and double click on TC icon
- select New from File menu
- select Save As from File menu
- name your program somename.c in the dialog box
- **type** the whole program
- select Save from File menu
- **to complie your program** select Compile from the Compile menu
- if compilation succeeds press any key and
- **to run your program** select Run from Run menu.

8.8.2 STEPS TO DO TO EXECUTE A C PROGRAM UNDER UNIX ENVIRONMENT:

- **to start terminal** right click on desktop,select terminal/console or goto applications->tools->terminals->click
- type vi somename.c then enter
- press i for insert mode
- **type** the whole program
- type :wq then enter to save the program
- **to compile** type cc somename.c then enter
- **to run** (on successful compilation) type ./a.out then enter.

8.8.3 THE C COMPILATION MODEL :

We will briefly highlight key features of the C Compilation model here.

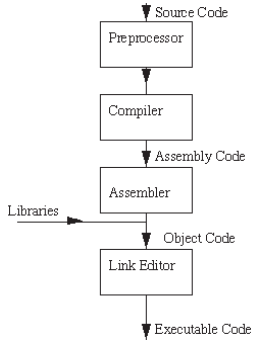


Fig. The C Compilation Model

The Preprocessor:

We will study this part of the compilation process in greater detail later. However we need some basic information for some C programs.

The Preprocessor accepts source code as input and is responsible for

- removing comments
- interpreting special *preprocessor directives* denoted by #.

For example

- #include -- includes contents of a named file. Files usually called *header* files. *e.g*
  - #include <math.h> -- standard library maths file.
  - #include <stdio.h> -- standard library I/O file
- #define -- defines a symbolic name or constant. Macro substitution.
  - #define MAX_ARRAY_SIZE 100

C Compiler:

The C compiler translates source to assembly code. The source code is received from the preprocessor.

Assembler:

The assembler creates object code. On a UNIX system you may see files with a `.o` suffix (`.OBJ` on MSDOS) to indicate object code files.

Link Editor:

If a source file references library functions or functions defined in other source files the *link editor* combines these functions (with `main()`) to create an executable file. External Variable references resolved here also.

EXERCISES

1. Give a brief introduction to C language.
2. Define constants and variables with examples.
3. List the C character set.
4. List the C keywords.
5. What is instruction and what are its types? Explain with examples.
6. Define a program. Explain with example the structure of a C program.
7. Describe the C compilation model.
8. What do you mean by C- tokens? **[RGU 2006]**
9. What are the rules for integer constants? **[RGU 2006]**
10. What are the variables? Give few valid and invalid variables. **[RGU 2006]**

CHAPTER 9

DATA TYPES

9.1 DATA TYPE :

A data type defines a set (domain) of legal values (data objects) along with some legal operations for manipulating them. Data types can be broadly categorized as elementary and secondary data types.

Elementary or Primary data types are those whose definitions are built into the language and are having direct hardware implementations.

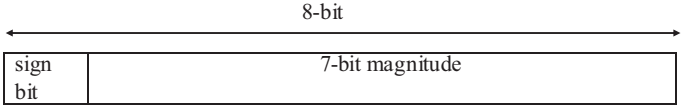
Secondary or Structured or User defined data types are those which are defined by the programmer using some facility provided by the language and their implementations in hardware

are not direct rather implemented using the implementations elementary data types by some arrangements facilited by the language and the system software.

9.2 ELEMENTARY DATA TYPES IN C:

Integers:

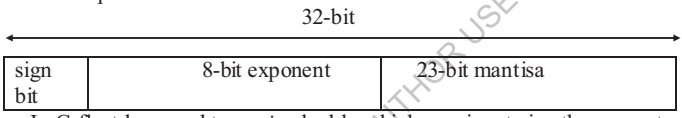
The data type integer written as int in C are whole numbers with a specific range of values.
e.g., for a 8-bit word length machine the range is -2^7 to +2^7-1 i.e. -128 to +127.



However C provides two other subtypes of int *viz.* short int represents small integer values that requires half the amount of storage normal int requires and long int that generally requires twice the amount.

Floats:

Floating point numbers are real numbers i.e. numbers having a decimal point; declared in C using keyword float.
e.g., a 32-bit representation of a float is as follows



In C float has a subtype *viz.* double which requires twice the amount of storage that of a normal float.

Characters:

In C the char keyword defines a character data type.The implementations (definition and storage) of characters are set to standards by different organizations, e.g., one such is ASCII(American Standard Code for Information Interchange) character set as shown below.

Table: ASCII Character Set

ASCII Value	Character (Description)	ASCII Value	Character (Description)
0	**NULL** (Null character)	64	@ (At sign)
1	**SOH** (Start of Header)	65	A (Capital A)
2	**STX** (Start of Text)	66	B (Capital B)
3	**ETX** (End of Text)	67	C (Capital C)
4	**EOT** (End of Transmission)	68	D (Capital D)
5	**ENQ** (Enquiry)	69	E (Capital E)
6	**ACK** (Acknowledgement)	70	F (Capital F)
7	**BEL** (Bell)	71	G (Capital G)
8	**BS** (Backspace)	72	H (Capital H)
9	**HT** (Horizontal Tab)	73	I (Capital I)
10	**LF** (Line feed)	74	J (Capital J)
11	**VT** (Vertical Tab)	75	K (Capital K)
12	**FF** (Form feed)	76	L (Capital L)

13	**CR**	(Carriage return)	77	M	(Capital M)
14	**SO**	(Shift Out)	78	N	(Capital N)
15	**SI**	(Shift In)	79	O	(Capital O)
16	**DLE**	(Data link escape)	80	P	(Capital P)
17	**DC1**	(Device control 1)	81	Q	(Capital Q)
18	**DC2**	(Device control 2)	82	R	(Capital R)
19	**DC3**	(Device control 3)	83	S	(Capital S)
20	**DC4**	(Device control 4)	84	T	(Capital T)
21	**NAK**	(Negative ack)	85	U	(Capital U)
22	**SYN**	(Synchronous idle)	86	V	(Capital V)
23	**ETB**	(End of transmision block)	87	W	(Capital W)
24	**CAN**	(Cancel)	88	X	(Capital X)
25	**EM**	(End of medium)	89	Y	(Capital Y)
26	**SUB**	(Substitute)	90	Z	(Capital Z)
27	**ESC**	(Escape)	91	[	(square brackets)
28	**FS**	(File separator)	92	\	(Backslash)
29	**GS**	(Group separator)	93	]	(square brackets)
30	**RS**	(Record separator)	94	^	(circumflex accent)
31	**US**	(Unit separator)	95	_	(underscore)
32		(space)	96	`	(Grave accent)
33	**!**	(exclamation mark)	97	a	(Lowercase a)
34	**"**	(Quotation mark)	98	b	(Lowercase b)
35	#	(Number sign)	99	c	(Lowercase c)
36	$	(Dollar sign)	100	d	(Lowercase d)
37	%	(Percent sign)	101	e	(Lowercase e)
38	&	(Ampersand)	102	f	(Lowercase f)
39	'	(Apostrophe)	103	g	(Lowercase g)
40	(	(parentheses)	104	h	(Lowercase h)
41	)	(parentheses)	105	**i**	(Lowercase i)
42	*	(Asterisk)	106	j	(Lowercase j)
43	+	(Plus sign)	107	k	(Lowercase k)
44	,	(Comma)	108	l	(Lowercase l)
45	-	(Hyphen)	109	m	(Lowercase m)
46	.	(Full stop , dot)	110	n	(Lowercase n)
47	/	(Slash)	111	o	(Lowercase o)
48	0	(number zero)	112	p	(Lowercase p)
49	1	(number one)	113	q	(Lowercase q)
50	2	(number two)	114	r	(Lowercase r)
51	3	(number three)	115	s	(Lowercase s)
52	4	(number four)	116	t	(Lowercase t)
53	5	(number five)	117	u	(Lowercase u)
54	6	(number six)	118	v	(Lowercase v)
55	7	(number seven)	119	w	(Lowercase w)
56	8	(number eight)	120	x	(Lowercase x)
57	9	(number nine)	121	y	(Lowercase y)
58	:	(Colon)	122	z	(Lowercase z)
59	;	(Semicolon)	123	{	(curly)
60	<	(Less-than sign)	124	|	(vertical slash)
61	=	(Equals sign)	125	}	(curly)
62	>	(Greater-than sign)	126	~	(Tilde ; swung dash)
63	?	(Question mark)	127	DEL	(Delete)

Table: Elementary C data types (on a 32-bit machine)

Data Type	Size in Bits	Range of values
char	8	-128 to +127
int	32	-2147483648 to 2147483647
float	32	3.4e-38 to 3.4e+38 (accuracy up to 7 digits)
double	64	1.7e-308 to 1.7e+308 (accuracy up to 15 digits)
void	0	Without value (null)

Table: Elementary C data types and modifiers (on a 32-bit machine)

Data Type	Size in Bits	Range of values
Char	8	-128 to +127
unsigned char	8	0 to 255
signed char	8	-128 to +127
int	32	-2147483648 to +2147483647
signed int	32	-2147483648 to +2147483647
unsigned int	32	0 to 4294967295
short	8	-128 to +127
short int	8	-128 to +127
signed short int	8	-128 to +127
unsigned short int	8	0 to 255
long	32	-2,147,483,648 to 2,147,483,647
long int	32	-2,147,483,648 to 2,147,483,647
unsigned long	32	0 to 4,294,967,295
signed long	32	-2,147,483,648 to 2,147,483,647
float	32	3.4e-38 to 3.4e+38
double	64	1.7e-308 to 1.7e+308 (accuracy up to 15 digits)
long double	80	3.4e-4932 to 1.1e+4932 (accuracy up to 19 digits)

Character Escape Sequences :

There are several character *escape* sequences which can be used in place of a character constant or within a string. They are:

Table: Escape Sequences

Escape sequence	Meaning
\a	alert (bell)
\b	backspace
\f	formfeed
\n	newline
\r	carriage return
\t	tab
\v	vertical tab
\\	backslash
\?	question mark
\'	quote
\"	double quote
ooo	character specified as an octal number
\x*hh*	character specified in hexadecimal

9.3 STRUCTERED DATA TYPES IN C:

Secondary or Structured or User defined data types are those which are defined by the programmer using some facility provided by the language and their implemantations in hardware are not direct rather implemented using the implementations elementary data types by some arrangements facilited by the language and the system software. e.g., arrays,structures, unions etc.

Array:

A group of related data items that share a common name is called an array. For example, we can define an array name marks to represent a set of marks obtained by a group of students. A particular value is indicated by writing a number called index number or subscript in brackets after the array name.

Example,

Marks[7]

Represents the marks of the 7th student. The complete set of values is referred to as an array, the individual values are called elements. The arrays can be of any variable type.

Structures:

Structures are variables that have several parts; each part of the object can havedifferent types. Each part of the structure is called a *member* of the structure.

There are two ways to declare structured variables. You can declare a type of yourown and use that type name to declare as many variables as you wish of that type, e.g.

```
struct date {
int day, month, year, yearday;
char monname[4];
};
struct date d;
struct date d1 = {4, 7, 1776, 186, "Jul"};
```

Unions:

A variable of union type may hold (at different times) objects of different types and sizes, the objects all occupying the same area of storage.


```
union tag {
members;
} variables;
For example:
union value {
int intval;
float fval;
char *pval;
} uval;
```

The variable uval can hold three different types of object, an int, a float or a string. It is the responsibility of the programmer to ensure that they access the variable in the appropriate manner.

Arrays,structures, unions etc. will be discussed in detail in later chapters.

EXERCISES

1. Define data type. What are different data types in C?
2. List the elementary data types in C.
3. Define structured data types and give examples.
4. Describe how floating point numbers can be represented.
5. What is ASCII character set. List the escape sequences of C.
6. Name and describe four basic data types in C? **[RGU 2006]**

7. Write a program to convert Fahrenheit to Celsius Equivalent. **[RGU 2006]**
8. Explain the following **[RGU 2006]**

    (a) escape sequence
    (b) standard library

CHAPTER 10

INPUT AND OUTPUT STATEMENTS

10.1 INPUT AND OUTPUT:

Input and output are functionalities to feed data to computer through input devices and get results to output devices respectively. These functionalities are provided by the system software. However languages like C provides facilities in terms of functions written by developers programmers to interact with these input/output functionalities of the system.

Various library functions are there in C for input and output. These are divided into the following major types –

1. Functions to interact with keyboard and visual display in required format called formatted console I/O functions.
   e.g., `printf() and scanf()`

```
int a;
printf("Enter the value of a");
scanf("%d",&a);
printf("The value of a is %d",a);
```


The printf conversion specifiers are listed below:

Table: printf conversion specifiers

Conversion Specifiers	Meaning of the output format
%c	Character
%d	Decimal integer
%e or %E	Scientific notation
%f	Floating point
%g or %G	Scientific notation or floating point (whichever shorter)
%i	Decimal integer
%o	Octal number
%p	Pointer
%s	String of characters
%u	Unsigned decimal integer
%x or %X	Hexadecimal number
%%	Display the % sign

2. Functions to interact with keyboard and visual display in predefined format called unformatted console I/O functions.
   e.g., `getch(), getche() , getchar(), gets(), putch(), putchar(), puts().`

```
char ch=getch();
putch(ch);
putchar(ch);
putch('b');
```

   input : a
   output: aab

3. Functions to interact with disk storage in the form of file operations called disk I/O functions.
   e.g., `fopen(), fgetc(), fclose().`
   Disk I/O functions will be discussed in detail later.

Example 1: My first C program

```
#include <stdio.h>

int
main (void)
{
   printf ("This is my first C program.\n");
   return (0);
}
```


This is my first C program.

Example 2: Trying printf and scanf

```
#include <stdio.h>

int
main (void)
{
   /* declarations */
   double x, y, z;

   /* executable statements */
   printf ("Enter two real numbers: ");
   scanf ("%lf %lf", &x, &y);
   z = x + y;
   printf ("\nThe sum of %lf and %lf is %f.\n", x, y, z);
   printf ("\nThe product of %lf and %lf is %lf.\n", x, y,
x*y);
```

```
   return (0);
}
```

Example 3: Numeric Placeholders

```
#include <stdio.h>

int
main (void)
{
   /* declarations */
   int a;
   double x;

   /* executable statements */
   a = 1000;
   x = 100.583665;

   printf ("%d\n", a);
   printf ("%3d\n", a);
   printf ("%4d\n", a);
   printf ("%5d\n", a);

   printf ("\n");

   printf ("%lf\n", x);
   printf ("%15lf\n", x);
   printf ("%15.4lf\n", x);
   printf ("%18.2lf\n", x);
   printf ("%12.0lf\n", x);

   return (0);
}
```



```
1000
1000
1000
 1000

100.583665
    100.583665
     100.5837
        100.58
       101
```

Example 4: This program reads four characters

```
#include <stdio.h>
```

```
int
main (void)
{
   /* declarations */
   char letter1, letter2, letter3, letter4;

   printf ("Enter a name: ");
   scanf ("%c%c%c%c", &letter1, &letter2, &letter3,
&letter4);
   printf ("You entered: %c%c%c%c", letter1, letter2,
letter3, letter4);
   printf (" / Backwards: %c%c%c%c\n", letter4, letter3,
letter2, letter1);

   return (0);
}
```

Enter a name: Lucy
You entered: Lucy / Backwards: ycuL

Example 5: The "circle" program (from keyboard)


```
#include <stdio.h>
#define PI 3.1416

int
main (void)
{
     /* declarations */
     double diam, area, circ, r;

     /* get diameter from user */
     printf ("Enter a value for the diameter: ");
     scanf ("%lf", &diam);

     /* do the computations */
     r = diam / 2;
     area = PI * r * r;
     circ = 2 * PI * r;

     /* display the report on the screen */
     printf ("\nA circle with a diameter of %3.1lf cm, ",
diam);
     printf ("has an area of %5.3lf cm2\n", area);
     printf ("and a circumference of %4.2lf cm.\n", circ);

     return (0);
}
```

Enter a value for the diameter: 10

A circle with a diameter of 10.0 cm, has an area of 78.540 cm2
and a circumference of 31.42 cm.

Example 6: The "circle" program (using files)

```
#include <stdio.h>
#define PI 3.1416

int
main (void)
{
     double diam, area, circ, r;
     FILE *in, *out;

     /* opening files */
     in = fopen ("diameter.data", "r");
     out = fopen ("report_circle.txt", "w");

     /* get diameter from file */
     printf ("Reading data from file...    ");
     fscanf (in, "%lf", &diam);
     printf ("Value read: %lf\n\n", diam);

     /* do the computations */
     r = diam / 2;
     area = PI * r * r;
     circ = 2 * PI * r;

     /* send results to report file */
     fprintf (out, "%4.2lf %4.2lf\n", area, circ);
     printf ("Sending results to file
report_circle.txt...\n\n");

     /* closing files */
     fclose (in);
     fclose (out);
     printf ("Program completed.");

     return (0);
}
```


Reading data from file... Value read: 10.400000

Sending results to file report_circle.txt...

Program completed.

Example 7: Program to show use of getchar() and putchar()

```
#include <stdio.h>

int
main (void)
{
```

```
    char c;

    printf ("Enter a character: ");
    /* getchar() gets a single character from the keyboard
*/
    c = getchar();

    printf ("The character is: ");
    /* putchar() prints a single character on the screen */
    putchar (c);

    return (0);
}
```

Enter a character: @
The character is: @

EXERCISES

1. Define input output functions.What are its different types? Give examples.
2. What is formatted and unformatted input output?
3. Show the use of getchar and putchar functions.
4. How a multicharacter string can be written using putchar?
5. Describe the use of printf and scanf functions.
6. List the format specifiers for printf function.

CHAPTER 11

OPERATORS, EXPRESSIONS AND ARITHMATICS

11.1 OPERATOR:

An operator is a symbol that directs the compiler to perform certain mathematical or logical manipulations. C has various operators of different types –

1. Assignment operator.
2. Arithmetic operators.
3. Bitwise operators.
4. Cast operators
5. Conditional operators.
6. Increment /Decrement and minus operators (unary).
7. Logical operators.
8. Relational operators.

1. Assignment Operator:

The operator = in C is called assignment operator is used to assign values to variables.

e.g.,
```
int a=5;
int b=6;
a=a+b;
```


The following operators are called compound assignment operators can also be used in C.

C has many assignment operators. Pascal and Fortran have one.

= assign
+= assign with add
-= assign with subtract
*= assign with multiply
/= assign with divide
%= assign with remainder
>>= assign with right shift
<<= assign with left shift
&= assign with bitwise AND
^= assign with bitwise XOR
|= assign with bitwise OR

All but the first assignment operator are shorthand methods of modifying a variable or object e.g.,

a=a+5; is written as a+=5; c=c/2; as c/=2; y=y%4; as y%=4;

The assign with operators come into their own where the specification of the object to be modified is long and complicated, and the chance for error in specifying it twice is large. As an example, consider the two statements below, both of which add one to a particular array element:

```
data[abs(nums[x%val])] = data[abs(nums[x%val])] + 1;
data[abs(nums[x%val])] += 1;
```

An expression that refers to a modifiable object must appear on the left hand side of each assignment operator. This is often simply the name of a variable, but as we will see later includes structure and union members, dereferenced pointers and elements of arrays. Such expressions are called modifiable lvalues. Assignment operators also produce expressions, thus a = b is an expression that has the same value as the value stored in a (which is not necessarily the value of b!) and has the same type as the type of a. This permits statements like:

```
a = b = c = d = e = 0;
```

An example of a situation where the type and value of the assignment expression is not the same as the value and type of the right hand operand, consider the following:

```
int main()
{
double x = 1.23, y;
int i;
y = i = x;
printf("%f\n", y);
return 0;
}
```

Here the assignment expression i = x has the int value 1, the double variable y has the value 1.0 after the assignment, not 1.23.

2. Arithmatic Operators:

Arithmatic operators can operate on any built in data types such as int,char,float.
Different arithmatic operators in C are

+	Addition
-	Subtraction
*	Multiplication
/	Division
%	Modulus

For modulus operator operand can not be a float.

The / operator is used for two different operations: integer and floating point division. If both operands of the divide operator are of integral (char, int and its derivatives) type then integer division is performed. If either operand is float , double or long double then real division is undertaken.

```
int main()
{
float a;
a = 1 / 3;
printf("%f\n", a);
return 0;
}
```

would print 0.000000 as integer division was performed even though a is of type float.

11.2 EXPRESSION :

An expression can be defined as follows

- a variable or a constant name is an expression.

- an expression connected to a unsigned vriable or constant by an arithmatic operator is an expression.
- an expression enclosed in parenthesis is an expression.
- two expressions connected by parenthesis is an expression.
- two arithmatic operators do not occur in succession in an expression.

e.g., `a`
`a+b`
`(a-b)`
`a*(a-b)`
`(a+b)*(a-c)` etc.

11.3 ASSOCIATIVITY AND ORDER OF PRECEDENCE OF ARITHMATIC OPERATORS :

In an arithmatic expression consisting of more than one arithmatic operators , their order of prcedence becomes important in order to get correct result.

e.g., +,- have same precedence.
*,/ have same precedence.
*,/ have higher precedence than +,-. So division or multiplication must be done before addition or subtraction.

11.4 ARITHMETIC CONVERSIONS :

Sometimes values within expressions are converted to another type, this is done to preserve information. For example, it is permitted to add a double to an int, the int value will be converted to a double before the addition takes place rather than vice versa. For every binary operator in an expression the following rules are used:

– if either operand is long double convert the other operand to long double
– otherwise, if either operand is double convert the other operand to double
– otherwise, if either operand is float convert the other operand to float
– otherwise perform integral promotions on both operands, and then:
– if either operand is unsigned long int convert the other to unsigned long int
– otherwise, if one operand is long int and the other is unsigned int then:
– if a long int can represent all values of unsigned int then
convert unsigned int operand to long int
– if a long int cannot represent all the values of unsigned int, then convert both operands to unsigned long int
– otherwise, if either operand is long int then convert the other to long int
– otherwise, if either operand is unsigned int then convert the other to unsigned int
– otherwise, both operands are of type int

Any value of type char or short int (signed or unsigned) is converted to a value of type int (if it can represent all the values of the original type) when it appears in an expression. If int cannot store all the values of the original type then unsigned int is used.

e.g., assuming the following declarations:
`char a, b;`
then
a + b has type int
`printf("%c",a);` the type of the second argument is int

Operator	Operand	Result
~	0010111	1101000
<<	0010111	0101110

>> 0010111 0001011

```
char a, b;
a=32;
b=76;
printf("%c",a+b); /* prints letter l (l=108) */
```

However, if a function prototype exists which states that the parameter is char then the promotion to int will not take place, e.g.

```
void fred(char c);
int main()
{
char a;
fred(a);
return 0;
}
```

The argument to fred will be of type char.

3. Bitwize Operators:

Bitwise operators allow manipulation of the actual bits held in each byte of a variable. Each byte consists of a sequence of 8 bits, each of which can store the value 0 or 1

Operator	Operation
~	one's complement
&	bitwise AND
^	bitwise XOR
|	bitwise OR
<<	left shift (binary multiply by 2)
>>	right shift (binary divide by 2)

Examples

AND	XOR	OR
0 & 0 = 0	0 ^ 0 = 0	0 | 0 = 0
1 & 0 = 0	1 ^ 0 = 1	1 | 0 = 1
0 & 1 = 0	0 ^ 1 = 1	0 | 1 = 1
1 & 1 = 1	1 ^ 1 = 0	1 | 1 = 1

e.g., to obtain the two separate bytes of a two byte int (int may be more than two bytes on your system, and not all computers have eight bit bytes, so this example is not universal):

```
hiByte = (i >> 8) & 0xFF;
loByte = i & 0xFF;
```

If i = 1011010100110111 then
i >>8 = 0000000010110101 (shift I right by 8 bits).
(i>>8) & OxFF ANDs 0000000010110101 with 0000000011111111 giving 10110101 (bits 9-16 of i)
i & 000000011111111 = 00110111 (bits 1-8 of i).

OxFF is the hexadecimal representation of 11111111 .

4. Cast Operators :

Cast operators allow the conversion of a value of one type to another.

e.g., (float) sum; converts type to float
(int) fred; converts type to int

5. Conditional operators :

The conditional operator is a symbolic form of the if-else staement in C represented by ?:

Example syntax is

```
c=(a>b)?a:b;
```

meaning if the condition a>b is true a is assigned to c otherwise b is assigned to c.

6. Increment/Decrement and minus operators :

These are unary operators i.e. associated with only one variable.

In C ++ increment (adds 1 to operand).
-- decrement (subtracts 1 from operand).

These operators can be used in prefix or postfix mode.

e.g., ++a or a++

But the difference is that prifix operator first adds 1 to the operand and the result is assigned to the variable on left whereas postfix operator first assigns the value to the variable on the left and then increments the operand.

e.g., int x=2;

a=x++;	a=++x;
a is 2	a is 3
x is 3	x is 3

Unary minus – negates the value of a constant or variable.

e.g., int a=5;
-a;
a is -5

7. Logical operators :

Symbols that are used to combine expressions containing relational operators are called logical operators. In situations where multiple conditions needs to be checked logical operators are used.

e.g., `((a>=6) && (b==5));`
The logical operators used in C are

&&	logical AND
||	logical OR
!	logical NOT

8. Relational operators :

Relational operators are used to test the relationship between variables or variables and constants.

e.g., a>b
c==10

Different relational operators in C are

==	equal to
>	greater than
<	less than
!=	not equal to
>=	greater than or equal to
<=	less than or equal to.

Table : Precedence and associativity of different operators

Operator	**Associativty**
() [] -> .	left to right
! ~ ++ -- + - * (*type*) sizeof	right to left
* / %	left to right
+ -	left to right
<< >>	left to right
< <= > >=	left to right
== !=	left to right
&	left to right
^	left to right
|	left to right
&&	left to right
||	left to right
?:	right to left
= += -= *= /= %= &= ^= |= <<= >>=	right to left
,	left to right

Example 1: The = operator puts the value on the right into the variable on the left .

```
#include <stdio.h>
int main (void)
{
     /* declarations */
     int a, b, c, d, e;

     /* fill variable a */
     a = 10;

     /* modify variable a few times*/
     a = 20;
     a = 10 + a;
     a = a + a + 2;
     a = 2 + a;

     /* a few more assignments */
     b = a;
     c = b = 5;
     c = 10 + a;
```

```
        d = a + a + 2;
        e = 20 + a;
        a = a - b + c;

        /* the final values are... */
        printf ("a:%4d\n b:%4d\n c:%4d\n d:%4d\n e:%4d\n", a,
    b, c, d, e);

        return (0);
    }
```

a: 133
b: 5
c: 74
d: 130
e: 84

Example 2: The remainder (%) operator.

```
    #include <stdio.h>

    int main (void)
    {
       int a, b, c, d;

       /* a few operations */
       a = 10 % 3;
       b = -10 % 3;
       c = 10 % -3;
       d = -10 % -3;

       /* you need to double the % to display on screen */
       printf ("10 %% 3 is %d\n", a);
       printf ("-10 %% 3 is %d\n", b);
       printf ("10 %% -3 is %d\n", c);
       printf ("-10 %% -3 is %d\n", d);

       return (0);
    }
```


10 % 3 is 1
-10 % 3 is -1
10 % -3 is 1
-10 % -3 is -1

Example 3: Integer division.

```
    #include <stdio.h>

    int
    main (void)
    {
```

```
   int a, b, c;
   double x, y, z, w;

   a = 10; b = 20;

   /* dividing two integers */
   z = a / b;
   c = a / b;
   printf ("The value of z is %5.3lf ", z);
   printf ("and the value of c is %d\n", c);

   /* converting (casting) one operand before the
division*/
   x = (double)a / b;
   printf ("The value of x is %5.3lf\n", x);

   /* casting the quotient after the division*/
   y = (double) (a / b);
   printf ("The value of y is %5.3lf\n", y);

   /* casting both operands before the division*/
   w = (double)a / (double)b;
   printf ("The value of w is %5.3lf\n", w);

   return (0);
}
```


The value of z is 0.000 and the value of c is 0
The value of x is 0.500
The value of y is 0.000
The value of w is 0.500

Example 4: The (-)unary operator

```
#include <stdio.h>

int main (void)
{
   int a, b, c;

   a = 10; b = 20;

   /* b is 20 so -b is -20 */
   b = -b + a;

   /* with multiple similar unary operators, use
parentheses */
   /* do you understand why c is 30? */
   c = -b - (-a) + -b;
   printf ("The value of b is %d ", b);
   printf ("and the value of c is %d\n", c);

   return (0);
```

```
}
```

The value of b is -10 and the value of c is 30

Example 5: Increment (++) and decrement (--).

```
#include <stdio.h>

int main (void)
{
   int a, b;

   a = 5;

   /* increment (++) */
   /* a is incremented by 1 */
   ++a;
   printf ("After ++a, a is now %d\n", a);

   /* a is once more incremented by 1 */
   a++;
   printf ("After a++, a is now %d\n", a);

   /* a is incremented but b gets the current a */
   b = a++;
   printf ("After b=a++, a is now %d and b is %d\n", a, b);

   /* a is incremented and b gets the incremented a */
   b = ++a;
   printf ("After b=++a, a is now %d and b is %d\n", a, b);

   /* decrement (--) */
   /* a is decremented by 1 */
   --a;
   printf ("After --a, a is now %d\n", a);

   /* a is once more decremented by 1 */
   a--;
   printf ("After a--, a is now %d\n", a);

   /* a is decremented but b gets the current a */
   b = a--;
   printf ("After b=a--, a is now %d and b is %d\n", a, b);

   /* a is decremented and b gets the decremented a */
   b = --a;
   printf ("After b=++a, a is now %d and b is %d\n", a, b);

   return (0);
}
```

```
After ++a, a is now 6
After a++, a is now 7
After b=a++, a is now 8 and b is 7
After b=++a, a is now 9 and b is 9
After --a, a is now 8
After a--, a is now 7
After b=a--, a is now 6 and b is 7
After b=++a, a is now 5 and b is 5
```

Example 6: The left shift bitwise operator .

```
#include <stdio.h>

int main (void)
{
    unsigned a=64, b=25, c=1, d=100;

    printf ("%4d << 1 = %4d (%3x HEX)\n", a, a<<1, a<<1);
    printf ("%4d << 1 = %4d (%3x HEX)\n", b, b<<1, b<<1);
    printf ("%4d << 1 = %4d (%3x HEX)\n", c, c<<1, c<<1);
    printf ("%4d << 1 = %4d (%3x HEX)\n", d, d<<1, d<<1);
    printf ("%4d << 2 = %4d (%3x HEX)\n", a, a<<2, a<<2);
    printf ("%4d << 3 = %4d (%3x HEX)\n", b, b<<3, b<<3);
    printf ("%4d << 4 = %4d (%3x HEX)\n", d, d<<4, d<<4);
    printf ("%4d << 5 = %4d (%3x HEX)\n", d, d<<5, d<<5);

    return(0);
}
```



```
 64 << 1 =  128 ( 80 HEX)
 25 << 1 =   50 ( 32 HEX)
  1 << 1 =    2 (  2 HEX)
100 << 1 =  200 ( c8 HEX)
 64 << 2 =  256 (100 HEX)
 25 << 3 =  200 ( c8 HEX)
100 << 4 = 1600 (640 HEX)
100 << 5 = 3200 (c80 HEX)
```

Example 7: The right shift bitwise operator.

```
#include <stdio.h>

int main (void)
{
    unsigned a=64, b=25, c=1, d=100;

    printf ("%4d >> 1 = %4d (%3x HEX)\n", a, a>>1, a>>1);
    printf ("%4d >> 1 = %4d (%3x HEX)\n", b, b>>1, b>>1);
    printf ("%4d >> 1 = %4d (%3x HEX)\n", c, c>>1, c>>1);
    printf ("%4d >> 1 = %4d (%3x HEX)\n", d, d>>1, d>>1);
    printf ("%4d >> 2 = %4d (%3x HEX)\n", a, a>>2, a>>2);
```

```
        printf ("%4d >> 3 = %4d (%3x HEX)\n", b, b>>3, b>>3);
        printf ("%4d >> 4 = %4d (%3x HEX)\n", d, d>>4, d>>4);
        printf ("%4d >> 5 = %4d (%3x HEX)\n", d, d>>5, d>>5);

        return(0);
    }
```

```
 64 >> 1 =  32 ( 20 HEX)
 25 >> 1 =  12 (  c HEX)
  1 >> 1 =   0 (  0 HEX)
100 >> 1 =  50 ( 32 HEX)
 64 >> 2 =  16 ( 10 HEX)
 25 >> 3 =   3 (  3 HEX)
100 >> 4 =   6 (  6 HEX)
100 >> 5 =   3 (  3 HEX)
```

EXERCISES

1. What is an operator? Describe different types of operators in C.
2. Define an operand?
3. Define an expression and describe the rules.
4. What is operator precedence and associativity?
5. Describe the arithmetic operators in C.
6. Show the use of logical operators.
7. Describe relational operators and their use.
8. Why do we use conditional operator? **[RGU 2006]**
9. Why do we are relational operator? List out them in C. **[RGU 2006]**

CHAPTER 12

SEQUENCE CONTROL STATEMENTS

12.1 SEQUENCE CONTROL :

A C program executes instructionwize sequentially until the sequential execution is disturbed explicitly. But all tasks cannot be performed using sequential executions, resulting into breaking the sequential execution by explicitly including program statements that changes the sequential flow of control to a directed flow of control. However to retain the imperative property of C language extreme effort had been made to design control structures in C so that even though the control flows from one point to a different specified point, after completion of execution of the specified part the flow of control returns to the point where from it was diverted. Even than some control statements such as goto, break violates this property of imperativeness. So in today's programming in C, programmers tries to avoid the use of these statements as far as possible.

Different types of control statements in C are

- decision control statements
  conditional branch e.g., if…else etc.
  - local unconditional jumps e.g., goto etc.
  - short circuit behavior e.g., ?: operator etc.
- case control statements e.g., switch…case etc.
- loop control statements e.g., while loop, for loop etc.
- subprogram control statements e.g., functions etc.

12.2 DECISION CONTROLS AND BRANCHING :

In situations where there is a need to disturb sequential flow of execution control branching is used. Branching can be

- conditional branch – branching is made after decision from a condition satisfaction called decision controls.
- unconditional branch –sudden branching without any conditions.

12.2.1 CONDITIONAL BRANCH (DECESION CONTROLS) :

In C the conditional branch or decesion control instructions are implemented using

- the if statement (one way branching)
- the if else statement (multiway branching)

One Way Branching – the if statement :

Branching is made after evaluating a condition; implemented in C using the if statement.

Syntax

```
if(<branch_condition_expression>)
{
     //statements
}
```

e.g.,

```
if(a>b)
{
     printf("a is larger");
}
```

Example 1: Write a program in C to print HELLO if the value of a specific variable is 1.

```
#include<stdio.h>
main()
{
int a;
printf("Enter the value of a :");
scanf("%d",&a);
if(a==1)
printf("HELLO\n");
}
```


Multiway Branching – the if…else statement :

Multiway branching is used in situations where we need to execute one out of many mutually exclusive actions. If there are two actions , it is called two way branching. In C it is implemented using the if…else statement.

Syntax :

```
if(<branch_condition_expression>)
{
     // statements
}
else
{
//  statements
}

if(<branch_condition_expression1>)
{
     // statements
}
else if(<branch_condition_expression2>)
{
     // statements
}
else if(<branch_condition_expression3>)
{
     // statements
}
else
{
```

```
     //  statements
     }
```

e.g.,
```
if(percentage>80)
     printf("Distinction");
else if(percentage>75)
     printf("Star");
else if(percentage>60)
     printf("First Division");
else if(percentage>45)
     printf("Second Division");
else if(percentage>30)
     printf("Third Division");
     else
          printf("Fail");
```

Example 2: Print the larger of two integers taken as input from keyboard.

```
#include<stdio.h>
main()
{
int a,b;
printf("Enter the values of a and b");
scanf("%d%d",&a,&b);
if(a>b)
printf("%d is larger",a);
else
printf("%d is larger",b);
}
```


Example 3: A simple if statement.

```
#include <stdio.h>

int main (void)
{
   int temp;

   printf ("What is the current temperature? ");
   scanf ("%d", &temp);
   printf ("-----------------------------------\n");

   /* this if statement contains a true and a false branch */
   /* with a compound statement in each branch*/
   if (temp >= 20)
   {
      printf ("The temperature is %d degrees. \n", temp);
      printf ("It is quite warm. \n");
   }
   else
   {
```

```
        printf ("The temperature is %d degrees. \n", temp);
        printf ("It is quite cool. \n");
    }


    return (0);
}
```

What is the current temperature? 13

The temperature is 13 degrees.
It is quite cool.

Example 4: Even vs. Odd .

```
#include <stdio.h>

int main (void)
{
    int number, even;

    /* ask user for number */
    printf ("Enter an integer number: ");
    scanf ("%d", &number);

    /* determine if number is even and put in variable */
    even = (number % 2 == 0);

    /* display report */
    if (even)
         printf ("%d is an even number.\n", number);
    else
         printf ("%d is an odd number. \n", number);

    return (0);
}
```


Enter an integer number: 56
56 is an even number.

Nested if statement :

If an if statement contains another if statement inside it , it is said to be nested if statement.

Example 5: Highest among three numbers.

```
#include<stdio.h>
main()
{
int a,b,c,high;
printf("Enter the three numbers");
```

```
scanf("%d%d%d",&a,&b,&c);
if(a>b)
     if(a>c)
     high=a;
else
     high=c;
else if(b>c)
     high=b;
else
     high=c;
printf("The highest number is : %d",high);
}
```

Multiple Conditions in if statement :

Using logical operators &&,||,! we can check multiple conditions in if statement.

Example 6: The traffic light program (nested ifs).

```
#include <stdio.h>

int main (void)
{
   char colour;

   /* ask user for colour */
   printf ("Enter the colour of the light (R, G or Y): ");
   scanf ("%c", &colour);

   /* test if colour is red */
   if (colour == 'r' || colour == 'R')
      printf ("STOP! \n");
   else
      if (colour == 'y' || colour == 'Y') /* yellow colour
test */
           printf ("CAUTION! \n");
      else
           if (colour == 'g' || colour == 'G') /* green colour
test */
              printf ("GO! \n");
           else
              /* if not Y or G or R then invalid colour */
              printf ("INVALID COLOUR! \n");

   return (0);
}
```


Enter the colour of the light (R, G or Y): G
GO!

12.2.2 LOCAL JUMPS — GOTO :

It is possible to jump to any statement within the same function using goto. A label is used to mark the destination of the jump. goto is rarely, if ever, needed, as if, switch , while and for should provide all the branching and iteration structures needed. However, there are times when a goto simplifies the code greatly. A frequently cited example is when something goes disastrously wrong deep within nested loops:

```
void fred(void)
{
while ( ... )
for( ... )
if (disaster) goto error;
error:
tidy up the mess
}
```

But in the example above, remember that the code could be rewritten as:

```
void fred(void)
{
while ( ... )
for( ... )
if (disaster)
{

tidy up the mess
return; /* and get out of here! */
}
}
```


12.2.3 SHORT CIRCUIT BEHAVIOUR :

Whenever expressions are connected together using the logical operators && (AND) or || (OR), only as many expressions as are needed to determine the overall logical value will be evaluated. This is known as short-circuit behaviour. For example, if two expressions are connected with && and the first expression is false, then it is guaranteed that the second expression will not be evaluated. The same is true of expressions connected with || where the first expression is true.

For example:

```
if (b != 0 && a / b > 1)
statement;
```

will prevent the evaluation of a / b if b is zero.

If the programmer accidentally uses & instead of && then the short-circuit behaviour is lost, which, in the example above may lead to a run-time division by zero error.

12.3 CONDITIONAL SELECTION (CASE CONTROL STATEMENTS) SWITCH…CASE :

Syntax

```
switch ( expression)
{
```

```
case value : statement; statement; ...
case value : statement; statement; ...
..
default : statement; statement; ...
}
```

switch is a mechanism for jumping into a series of statements, the exact starting point depending on the value of the expression. In the example below, for example, if the value 3 is entered, then the program will print three two one something else!

```
int main()
{
int i;
printf("Enter an integer: ");
scanf("%d",&i);
switch(i)
{
case 4: printf("four ");
case 3: printf("three ");
case 2: printf("two ");
case 1: printf("one ");
default: printf("something else!");
}
return 0;
}
```


This may not be what was intended. This process of executing statements in subsequent case clauses is called fall through. To prevent fall through, break statements can be used, which cause an immediate exit from the switch statement. In the example above, replacing

case 4: printf("four ");

with

case 4: printf("four "); break;

and adding break statements to the statements for the other labels, will result in a program that prints only one string depending on the value of the integer input by the user. The values listed in the case part of the switch statement must be constant integer values; integer expressions can be used as long as the value can be determined at compile time.

The default label is optional, but if it is present acts as a catch all clause. The labels can occur in any order; there is no need to have the default label last, for example (but it usually reads better if it is!).

Example 7: The traffic light program (switch).

```
#include <stdio.h>

int main (void)
{
   char colour;

   /* ask user for colour */
   printf ("Enter the colour of the light (R,G,Y,A): ");
   scanf ("%c", &colour);
```

```
    /* test the alternatives */
    switch (colour)
    {
        /* red light */
        case 'R':
        case 'r':
                  printf ("STOP! \n");
                  break;

        /* yellow or amber light */
        case 'Y':
        case 'y':
        case 'A':
        case 'a':
                  printf ("CAUTION! \n");
                  break;

        /* green light */
        case 'G':
        case 'g':
                  printf ("GO! \n");
                  break;

        /* other colour */
        default:
                  printf ("The colour is not valid.\n");
    }

    return (0);
}
```



```
Enter the colour of the light (R,G,Y,A): G
    GO!
```

12.4 LOOP CONTROL STATEMENTS :

12.4.1 ITERATION — WHILE, FOR :

while loop :

Syntax

```
while ( expression) /* while expression is true do*/
statement; /* statement
*/
do /* do */
statement; /* statement */
while ( expression); /* while expression is true
*/
```

for loop :

Syntax

```
for (expr1; expr2; expr3)
statement;
expr1; /* equivalent (almost) to above */
```

```
while ( expr2) /* for loop */
{
statement;
expr3;
}
```

The difference between the while and the do-while loops is the location of the test. With a while loop the test is made before the statement that forms the body of the loop is executed; it is possible that the statement is never executed. With the do while loop, the statement will always be executed at least once; the value of the expression then determines if the statement is executed again. for loops behave (more or less) like the equivalent while loop shown in the generic example above. The first expression is executed as a statement first, the second expression is then tested to see if the body of the loop should be executed. The third expression is executed at the end of every iteration of the loop. An example for loop, to execute a statement 10 times 4, is given below:

```
for (i = 0; i < 10; i++)
printf("%d\n",i);
```

An alternative way of executing a statement n times is:

```
i = n;
while (i--)
statement;
```


If you use this method, make sure that n is greater than zero, or make the test i-- > 0. Any of the three expressions in the for loop can be omitted. Leaving out the first or the third expressions means that no additional action is performed either before the loop starts or after each iteration. Omitting the second expression results in a loop that will always execute, the value of the controlling expression is assumed to be true. If any expression is omitted, the separating semi-colons must still be included. The following for loop does nothing before it starts, performs no additional action after each iteration and will continue forever!

```
for (;;) /* do forever */
printf("hello\n");
```

The following two statements can be used within any of the three loops we have seen to add additional control over the execution of the loop. Normally, they are used to abort a process if something has gone wrong.

break exits immediately innermost enclosing loop
continue go immediately to next iteration of loop
When continue is used in a for loop, the third expression in the control statement is guaranteed to be executed. This behaviour is different from the “equivalent” while loop.

Example 8: A simple count from 1 to 100 .

```
#include <stdio.h>

int main (void)
{
   int n;
```

```
   n = 1; /* loop initialization */

   /* the loop */
   while (n <= 100) /* loop condition */
   {
      printf ("%d ", n); /* loop body */
      n = n + 1; /* loop update */
   }

   return (0);
}
```

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47
48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69
70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91
92 93 94 95 96 97 98 99 100

Example 9: Mission to the Moon.


```
#include <stdio.h>

int main (void)
{
   double transit, period, time;
   int n_orbits, orbit;

   /* 73 hours from Earth to Moon */
   transit = 72;

   /* 1.5 hours per orbit around Moon */
   period = 1.5;

   /* mission begins */
   printf ("Mission to the Moon - Times in hours\n");
   printf ("====================================\n");
   time = 0.0;
   n_orbits = 10; /* mission is 10 orbits */
   printf ("Time - %4.1lf - Mission begins\n", time);

   /* we are at the moon */
   time = time + transit;
   printf ("Time = %4.1lf - At the moon\n", time);
   orbit = 1;

   /* doing the orbits around the Moon */
   while (orbit <= n_orbits)
   {
      time = time + period;
      printf ("Time = %4.1lf - %2d orbits completed\n",
time, orbit);
      orbit = orbit + 1;
```

```
    }

    /* back to Earth */
    time = time + transit;
    printf ("Time = %5.1lf - Mission complete.\n", time);

    return (0);
}
```

Mission to the Moon - Times in hours
==========
Time - 0.0 - Mission begins
Time = 72.0 - At the moon
Time = 73.5 - 1 orbits completed
Time = 75.0 - 2 orbits completed
Time = 76.5 - 3 orbits completed
Time = 78.0 - 4 orbits completed
Time = 79.5 - 5 orbits completed
Time = 81.0 - 6 orbits completed
Time = 82.5 - 7 orbits completed
Time = 84.0 - 8 orbits completed
Time = 85.5 - 9 orbits completed
Time = 87.0 - 10 orbits completed
Time = 159.0 - Mission complete.

Example 10: The fuel tank program.

```
#include <stdio.h>

int main (void)
{
    double capacity, supply, pumped; /* in liters */

    /* initialize capacity of tank */
    capacity = 5000.0;

    /* ask user for initial supply already in tank */
    printf ("Enter the the initial supply: ");
    scanf ("%lf", &supply);

    /* the program loops until supply falls below 10% */
    while (supply > capacity * 0.10)
    {
        /* ask user for quantity removed or delivered */
        printf ("\nEnter the amount delivered(+)/removed(-):
");
        scanf ("%lf", &pumped);
        supply = supply + pumped;

        /* test so that you don't pump more when tank is empty */
        if (supply < 0.0)
           supply = 0.0;
```

```
        /* test so that you don't fill more when tank is full */
        if (supply > capacity)
           supply = capacity;
    }

        printf ("\nSupply below 10%% (%.2lf l remaining)\n",
supply);

        return (0);
}
```

Enter the the initial supply: 2000

Enter the amount delivered(+)/removed(-): -900

Enter the amount delivered(+)/removed(-): 1100

Enter the amount delivered(+)/removed(-): -1400

Enter the amount delivered(+)/removed(-): -200

Enter the amount delivered(+)/removed(-): -250

Supply below 10% (350.00 l remaining)

Example 11: Input validation loop (do-while).

```
#include <stdio.h>

int main (void)
{
   char colour;

   /* ask user for colour */
do
{
   printf ("Enter the colour of the light (R,G,Y,A): ");
   scanf (" %c", &colour); /* very important to leave space
before %c here */

}while (colour!='R' && colour!='r' && colour!='G' &&
colour!='g'
 && colour!='Y' && colour!='y' && colour!='A' &&
colour!='a');

   /* test the alternatives */
   switch (colour)
   {
       /* red light */
       case 'R':
       case 'r':
                 printf ("STOP! \n");
```

```
                    break;

            /* yellow or amber light */
            case 'Y':
            case 'y':
            case 'A':
            case 'a':
                    printf ("CAUTION! \n");
                    break;

            /* green light */
            case 'G':
            case 'g':
                    printf ("GO! \n");
                    break;

            /* no default case necessary here */
        }

        return (0);
    }
```

Enter the colour of the light (R,G,Y,A): b
Enter the colour of the light (R,G,Y,A): x
Enter the colour of the light (R,G,Y,A): G
GO!

Example 12: Simple countdown using a for loop.

```
#include <stdio.h>

int main (void)
{
    int time;

    /* the loop */
    for (time=60; time>=0; time=time-1)
    {
       printf ("%d  ", time);
    }

    printf ("\n\nLIFTOFF!\n\n");

    return(0);
}
```

60 59 58 57 56 55 54 53 52 51 50 49 48 47 46
45 44 43 42 41 40 39 38 37 36 35 34 33 32 31
30 29 28 27 26 25 24 23 22 21 20 19 18 17 16
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0

LIFTOFF!

12.5 SUBPROGRAM SEQUENCE CONTROL STATEMENTS:

12.5.1 FUNCTIONS-BUILDING BLOCKS OF PROGRAMS :

All C programs consist of one or more functions. Functions are the building blocks of a program. All functions are at the same level — there is no nesting. One (and only one) function must be called main.

Return Value :

All functions can return a value, including main.Functions can return arithmetic values (int, float etc.), structures, unions, pointers or void. If the return type is specified as being void, then no value is returned by the function. Functions cannot return a function or an array. For functions that will return a value, the return statement is used in conjunction with an expression of an appropriate type. This causes immediate termination of the function, with the value of the expression being returned to the caller. return can also be used with functions of type void, but no return value can be specified.

Function Parameters :

All functions (including main) can accept parameters.The example below shows the old Kernighan & Ritchie C function definition format.


```
double minimum(x, y)
double x, y;
{
if (x < y)
return x;
else
return y;
}
```

ANSI C will accept this old style definition, but introduces a newer, safer, definition format:

```
double minimum(double x, double y)
{
if (x < y)
return x;
else
return y;
}
```

In both cases the parameter list must be specified, and their types must be declared. The parameters to the function (the expressions given in the function call) are passed by value only. If, in a new style definition, the parameter list contains the single word void, then the function does not take any parameters. It is common to call the variables specified in the function definition parameters and the expressions given in a function call arguments. For example, in the following call of minimum , the expressions a and b * 2 are the arguments to the function. The values of the two expressions will be copied into the parameters x and y. Sometimes the terms formal argument and actual argument are used instead; the formal argument being the variable given in the function definition, the actual argument being the expression given in the function call.

```
minimum(a, b*2);
```

Variable Function Parameters :

All function parameters are passed by value. To make a function alter a variable, the address of the variable must be passed, i.e. pass the variable by reference.

```
int max(int a, int b, int *c);
int main()
{
int x = 4, y = 5, z;
max(x, y, &z); /* generate a pointer to z */
return 0;
}
int max(int a, int b, int *c)
{
if (a > b)
*c = a; /* *c modifies the variable */
else /* whose address was passed */
*c = b; /* to the function */
}
```


Function Definition and Declaration :

A function definition is where the function name, parameters, code and return type are specified. A function declaration is where the name and return type of a function are given. The definition of a function includes a declaration of that same function implicitly.
A function can be declared many times (as long as the declarations declare the function to be of the same type) but can only be defined once. Declarations of functions are sometimes necessary to appease the compiler, which always assumes, if the information is not available, that all functions return int.

```
/* declaration of minimum() */
double minimum(double x, double y);

int main()
{
printf("%f\n", minimum(1.23, 4.56));
return 0;
}
/* definition of minimum() */
double minimum(double x, double y)
double x, y;
{
if (x < y)
return x;
else
return y;
}
```

The problem could also be solved by placing the function definition before the call to the function.

Function Prototypes :

The ANSI C standard introduces function prototypes. An example is given below. It also allows function definitions to be written in the same form as the new prototypes.

```
double minimum(double, double);
/* prototype of minimum() */
int main()
{
printf("%f\n", minimum(1.23, 4.56));
return 0;
}
double minimum(double x, double y)
/* definition of minimum() */
{
if (x < y)
return x;
else
return y;
}
```

The use of prototypes or the new style function definition allows the compiler to check that the parameters to a function are sensible (not necessarily the same), as well as checking the return type of the function; but only if the definition or prototype appears before the function call.

ANSI C draws a distinction between the following two statements. The first is afunction declaration stating that fred takes an, as yet, unspecified number of parameters. The second is a function prototype which states that jim takes no parameters.

```
double fred(); /* declaration */
double jim(void); /* prototype */
```

12.5.2 RECURSION :

C functions may be used recursively; that is, a function may call itself either directly or indirectly. Consider printing a number as a character string. As we mentioned before, the digits are generated in the wrong order: low-order digits are available before high-order digits, but they have to be printed the other way around. There are two solutions to this problem. On is to store the digits in an array as they are generated, then print them in the reverse order. The alternative is a recursive solution, in which printd first calls itself to cope with any leading digits, then prints the trailing digit. Again, this version can fail on the largest negative number.

```
#include <stdio.h>
/* printd: print n in decimal */
void printd(int n)
{
if (n < 0) {
putchar('-');
n = -n;
}
if (n / 10)
```

```
printd(n / 10);
putchar(n % 10 + '0');
}
```

When a function calls itself recursively, each invocation gets a fresh set of all the automatic variables, independent of the previous set. This in printd(123) the first printd receives the argument n = 123. It passes 12 to a second printd, which in turn passes 1 to a third. The third-level printd prints 1, then returns to the second level. That printd prints 2, then returns to the first level. That one prints 3 and terminates. Another good example of recursion is quicksort, a sorting algorithm developed by C.A.R. Hoare in 1962. Given an array, one element is chosen and the others partitioned in two subsets - those less than the partition element and those greater than or equal to it. The same process is then applied recursively to the two subsets. When a subset has fewer than two elements, it doesn't need any sorting; this stops the recursion.

Our version of quicksort is not the fastest possible, but it's one of the simplest. We use the middle element of each subarray for partitioning.

```
/* qsort: sort v[left]...v[right] into increasing order */
void qsort(int v[], int left, int right)
{
int i, last;
void swap(int v[], int i, int j);
if (left >= right) /* do nothing if array contains */
return; /* fewer than two elements */
swap(v, left, (left + right)/2); /* move partition elem */
last = left; /* to v[0] */
for (i = left + 1; i <= right; i++) /* partition */
if (v[i] < v[left])
swap(v, ++last, i);
swap(v, left, last); /* restore partition elem */
qsort(v, left, last-1);
qsort(v, last+1, right);
}
```


We moved the swapping operation into a separate function swap because it occurs three times in qsort.

```
/* swap: interchange v[i] and v[j] */
void swap(int v[], int i, int j)
{
int temp;
temp = v[i];
v[i] = v[j];
v[j] = temp;
}
```

The standard library includes a version of qsort that can sort objects of any type. Recursion may provide no saving in storage, since somewhere a stack of the values being processed must be maintained. Nor will it be faster. But recursive code is more compact, and often much easier to write and understand than the non-recursive equivalent. Recursion is especially convenient for recursively defined data structures like trees.

EXERCISES

1. Discuss with the help of suitable examples the working of three looping structures available in C language. **[NEHU 2008]**

2. Find out the output of the following program segments: **[NEHU 2008]**

   (i)
   ```
   int i = 5;
   while (i > 0)
   printf ("%d", i);
   ```

   (ii)
   ```
   int j=5;
   if (i = 0 || j<0 )
   printf ("Hello");
   else
   printf("World");
   ```

   (iii)
   ```
   int i=1;
   switch(i)
   {
   default: printf("1");
   case1: printf("2");
   case1: printf("123");
   }
   ```


3. Explain nested if else structure. **[RGU 2006]**

4. Write the program weather the given leap year or not? **[RGU 2006] [GIMT(GU) 2009]**

5. Difference between break and continue statements? **[RGU 2006]**

6. Write the output of the following program segments **[RGU 2006]**

```
main()
{
int i = 0;
while(i++ <10)
     printf("CSE");
printf("%d = %d", i);
}
```

7. Write the program weather the given number is prime or not? **[GIMT(GU) 2008]**

8. Write a program to simulate a simple arithmetic calculator using switch case. Operation supported are +.-,* and /.**[GIMT(GU) 2008]**

CHAPTER 13

ARRAYS, POINTERS, STRINGS AND FUNCTIONS

13.1 ARRAYS:

13.1.1 THE MEANING OF AN ARRAY:

A group of related data items that share a common name is called an array. For example, we can define an array name marks to represent a set of marks obtained by a group of students. A particular value is indicated by writing a number called index number or subscript in brackets after the array name.

Example,

Marks[7]

Represents the marks of the 7th student. The complete set of values is referred to as an array, the individual values are called elements. The arrays can be of any variable type.

One-dimensional array:

When a list of items can be given one variable name using only one subscript and such a variable is called a single-subscripted variable or one dimensional array.

In C language ,single-subscripted variable xi can be represented as

```
x[1],x[2],x[3].....x[n]
```

The subscripted variable xi refers to the ith element of x. The subscript can begin with number 0. For example, if we want to represent a set of five numbers, say (57,20,56,17,23), by a array variable num, then we may declare num as follows

Int Num[5];

And the computer reserves five storage locations as shown below:

The values can be assigned as follows:

Num[0]=57;
Num[1]=20;
Num[2]=56;
Num[3]=17;
Num[4]=23;

The table below shows the values that are stored in the particular numbers.

Num[0]
Num[1]
Num[2]

Num[3]
Num[4]

57
20
56
17
23

Two dimensional arrays:

There are certain situations where a table of values will have to be stored. C allows us to define such table using two dimensional arrays.

Two dimensional arrays are declared as follows:

Type array_name [row_size][column_size]

In c language the array sizes are separated by its own set of brackets.

Two dimensional arrays are stored in memory as shown in the table below. Each dimension of the array is indexed from zero to its maximum size minus one; the first index selects the row and the second index selects the column within that row.

	Column0	Column1	Column2
	[0][0]	[0][1]	[0][2]
Row 0	210	340	560
	[1][0]	[1][1]	[1][2]
Row 1	380	290	321
	[2][0]	[2][1]	[2][2]
Row2	490	235	240
Row3	[3][0]	[3][1]	[3][2]
	240	350	480

13.1.2 DECLARATION AND INITIALIZATION OF ARRAYS:

The arrays are declared before they are used in the program. The general form of array declaration is

Type variable_name[size];

The type specifies the type of element that will be contained in the array, such as int,float,or char and the size indicates the maximum number of elements that can be stored inside the array.

For Example:

Float weight[40]

Declares the weight to be an array containing 40 real elements. Any subscripts 0 to 39 are valid.

Similarly,

Int group1[11];

Decalres the group1 as an array to contain a maximum of 10 integer constants.

The C language treats character strings simply as arrays of characters. The size in a character string represents the maximum number of characters that the string can hold.

For example:

Char text[10];

Suppose we read the following string constant into the string variable text.

"HOW ARE YOU"

Each character of the string is treated as an element of the array text and is stored in the memory as follows.

'H'
'O'
'W'
'A'
'R'
'E'
'Y'
'O'
'U'
'\o'

When the compiler sees a character string, it terminates it with an additional null character. Thus, the element text[11] holds the null character '\o' at the end. When declaring character arrays, we must always allow one extra element space for the null terminator.

13.1.3 INITIALIZATION OF ARRAYS:

The general form of initialization of arrays is:

Static type array-name[size]={ list of values};

The values in the list are separated by commas.

For example, the statement below shows
Static int num[3]={2,2,2};

Will declare the variable num as an array of size 3 and will assign two to each element. If the number of values is less than the number of elements, then only that many elements will be initialized. The remaining elements will be set to zero automatically.

For example:
Static float num1[5]={0.1,2.3,4.5};
Will initialize the first three elements to 0.1,2.3 and 4.5 and the remaining two elements to zero. The word static used before type declaration declares the variable as a static variable.
In some cases the size may be omitted. In such cases, the compiler allocates enough space for all initialized elements.

For example, the statement
Static int count[ ]= {2,2,2,2};
Will declare the counter array to contain four elements with initial values 2.

Character arrays may be initialized in a similar manner. Thus, the statement
Static char name[ ]={ 'S 'W,'A,'N}
Declares the name to be an array of four characters, initialized with the string "SWAN"

There certain draw backs in initialization of arrays.
1. There is no convenient way to initialize only selected elements.
2. There is no shortcut method for initializing a large number of array elements.

Reading Writing and manipulation of above types of arrays.

Example 1: Program showing one-dimensional array

```
main()

{
     int i;
     float a[10],value1,total;
     printf("Enter 10 Real numbers\n");
     for(i=0;i<10;i++)
{
     scanf("%f", &value);
     x[i]=value1;
}

total=0.0;
for(i=0;i<10;i++)
total=total+a[i]*a[i];

printf("\n");
for(i=0;i<10;i++)
printf("x[%2d]= %5.2f\n", i+1, x[i]);
```

```
printf("\ntotal=%.2f\n", total);
}
```

Example 2: Program to read and write two dimensional arrays.

```
#include<stdio.h>
main()
{
     int a[10][10];
            int i, j row,col;
     printf("\n Input row and column  of a matrix:");
     scanf("%d %d",  &row,&col);
     for(i=0; i<row;i++)
     for(j=0;j<col;j++)
     scanf("%d", &a[i][j]);
for(i=0;i<row;i++)
           {
     for(j=0;j<col;j++)
     printf("%5d", a[i][j]);
            printf("\n");
           }
```


Example 3: Program to print multiplication tables.

```
#define R1   4
#define  C1   4

main()
{
     int row,col,prod[R1][C1];
            int i,j;
     printf(" MULTIPLICATION TABLE \n\n");
     printf("   ");

     for(j=1;j<=C1;j++)
       printf("%4d",j);
       printf("\n");
        printf("-----------------------------------------
\n");
       for(i=0;i<R1;i++)
        {
          row=i+1;
          printf("%2d|", R1);
       for(j=1;j<=C1;j++)
         {
          col=j;
          prod[i][j]=row*col;
          printf("%4d", prod[i][j]);
                 }
          printf("\n");
              }
     }
```

Output

```
        MULTIPLICATION TABLE
        1  2   3   4
   ----------------------------------------
1   |    1   2   3   4
2   |    2   4   6   8
3   |    3    6  9   12
4   |    4    8  12  16
```

Example 4: Write a C program to convert a binary number to decimal number using one-dimensional array.

```
#include<stdio.h>
#include<math.h>
 main()
{
int b[10],sum=0,i,dig;
printf("\n enter the number of digits (MAX 8): \t");
scanf("%d", &dig);
printf("\n Enter the binary digits (Left to Right): \t");
for(i=1;i<=dig;i++)
     scanf("%d", &bin[i]);
for(i=dig;i<=1;i--)
sum+=bin[i]*pow(2,dig-1);
printf("\n the decimal number is= \t %d n", sum);
}
```


Example 5: Program to calculate the total cost of tubes.

```
#include<stdio.h>
main()
{
     int st[5], watt;
     float cost[5], total;
     total=0;

for(watt=0;watt<=4;++watt)
  {
     scanf("%d %f", &st[watt], &cost[watt])
     {
          scanf("%d  %f",  &st[watt], &cost[watt]);
          total+= (float) st[watt]*cost[watt];
     }
printf("%f \n", total);
}
```

Example 6: Program to show swapping of numbers.

```
#include<stdio.h>
main()
{
     int x[10], i, j, temp;
     for(i=0;i<=9;++i)
     scanf("%d", &x[i]);
for(j=0;j<=8;j+=2)
     {
     temp=x[j];
     x[j]=x[j+1];
    x[j+1]=temp;
}

for(i=0;i<=9;++i)
printf("%d", x[i]);
printf("\n");
}
```

Example 7: Program to sort a list of numbers:


```
#define N 10
     main()
{
     int i,j,k;
float a[N],t;
printf("Enter the number of items\n");
scanf("%d", &n);
printf("Input %d values \n", n);
for(i=1; i<=n ;;i++)
  scanf("%f", &a[i]);
for(i=1;i<=n-1;i++)
{
   for(j=1;j<=n-i; j++)
     {
         if)a[j]<=a[j+1])
{
     t=a[j];
     a[j]=a[j+1];
     a[j+1]=t;
}
else
     continue;
}
}
for(i=1;i<=n;i++)
 printf("%f", a[i]);
}
```

Example 8: Program to calculate standard deviation

```
#include<math.h>
#define MAX 100
```

```
main()
{
     int i,n;
float val[MAX],deviation,sum,ssqr,mean,var,stddev;
sum=ssqr=n=0;
printf("Input values: input-1 to end\n");
for(i=1;i<MAX;i++)
{
     scanf("%f", &val[i]);
     if(val[i]==-1)
        break;
     sum+=val[i];
     n+=1;
}

mean=sum/(float)n;
for(i=1;i<=n;i++)
{
     deviation=val[i]-mean;
     ssqr+=deviation*deviation;
}
 var=ssqr/(float)n;
stddev=sqrt(var);
printf("\n Number of items:%d\n",n);
printf("Mean: %f \n", mean);
printf("Standard deviation: %f\n", stddev);
}
```


Example 9: Program to find the largest and smallest of numbers:

```
#include<stdio.h>
main()
{
     int I,s, largcount,smcount;
     float num[30],lar,small;

printf("\n size of array (MAX 30): \t");
scanf("%d", &size);

printf("\n Array elements:\t");

for(i=0;i<size;i++)
     scanf("%f", &num[i]);

for(i=0;i<size;i++)
     printf("%f", &num[i]);

lar=small=num[0];
larcount=smcount=1;
for(i=1;i<size;i++)
{
     if(num[i]>lar)
{
```

```
     lar=num[i];
     larcount=i+1;
}

elseif(num[i]<small)
{
     small=num[i];
     smcount=i+1;
}
}
printf(“\n Largest value is % f found at %d”,
lar,larcount);
printf(“\n Smallest value is %f found at %d “, small,
smcount);
}
```

Example 10: This program initializes an array with all cells filled with 0.0.

```
#include <stdio.h>

int main (void)
{

     double x[100];
     int i;

     /* initializing the array with 0.0 */
     for (i=0; i<100; ++i)
          x[i] = 0.0;


     /* printing the array for verification */
     for (i=0; i<100; ++i)
          printf ("%5.1lf", x[i]);

     return (0);
}
```

```
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
0.0 0.0 0.0 0.0
```

Example 11: This program asks the user for a value and fills all 100 cells of an array with that value.

```
#include <stdio.h>
```

```
/* no size in array parameter */
/* just a pointer to array in main */
void
fill_array (int list[], int n, int in_value)
{
     int i;
     for (i=0; i<n; ++i)
          list[i] = in_value;
}

int
main (void)
{

     int x[100], i, value;

     /* initializing the array with a user value */
     /* the 2nd argument must be the size of the array */
     printf ("Enter a value: ");
     scanf ("%d", &value);
        fill_array (x, 100, value);


     /* printing the array for verification */
     for (i=0; i<100; ++i)
          printf ("%d  ", x[i]);

     return (0);
}
```



```
5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
```

Example 12: This program computes the mean and standard deviations of the values inside an array .

```
#include <stdio.h>
#include <math.h>
#define MAX 5

int
main (void)
{

     double mean, sd, sum, sumsq;
     double x[] = {10.0, 15.0, 20.0, 10.0, 30.0};
     int i;
```

```
        sum = 0;
        sumsq = 0;

        /* computing the sum and sum of squares */
        for (i=0; i<MAX; ++i)
        {
             sum = sum + x[i];
             sumsq = sumsq + x[i] * x[i];
        }


        /* computing mean and standard deviation */
        mean = sum / MAX;
        sd = sqrt(sumsq / MAX - mean * mean);


        /* printing report */
        printf ("The mean is %lf. \n", mean);
        printf ("The standard deviation is %lf. \n", sd);

        return (0);
}
```


The mean is 17.000000.
The standard deviation is 7.483315.

Example 13: This program fills an array from a file.

```
#include <stdio.h>

int
main (void)
{
     int numbers[10], i;
     FILE *input;

     input = fopen("numbers.txt", "r");

     /* reading file - filling array */
     for (i=0; i<10; ++i)
          fscanf(input, "%d", &numbers[i]);


     /* printing the content of array */
     printf("The numbers read are: ");
     for (i=0; i<10; ++i)
          printf("%4d", numbers[i]);

     printf ("\n");
```

```
        fclose (input);

        return (0);
    }
```

The numbers read are: 43 56 23 87 123 13 77 41 9 10

Example 14: This programs fills an array with a value submitted by the user.

```
    #include <stdio.h>

    /* array parameter can be expressed as a pointer */
    /* *list is the same thing as list[] */
    void
    fill_array (int *list, int n, int in_value)
    {
        int i;
        for (i=0; i<n; ++i)
            list[i] = in_value;
    }

    int
    main (void)
    {

            int x[100];
            int i;

        /* &x[0] is the address of the x[0] */
        /* which is the same thing as x */
           fill_array (&x[0], 100, 5);


        /* printing the array for verification */
        for (i=0; i<100; ++i)
            printf ("%d  ", x[i]);

        return (0);
    }
```

```
5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
5 5 5 5 5 5 5 5 5 5 5 5
```

Example 15: This program partially fills an array from a file until the end of file (EOF). We get the actual number of data read

```
#include <stdio.h>

int
array_from_file (double a[], int size)
{
        int i;
        FILE* in;

        in = fopen ("data_array.dat", "r");

        i=0; /* the first cell */

        /* filling the array cell by cell */
        /* until it is full or until the EOF */
        while (i < 100 && fscanf (in, "%lf", &a[i]) != EOF)
        {
               i=i+1;
        }

        fclose (in);

        /* the actual number of values in the array */
        return (i);
}


int
main (void)
{
         double array[100];
        int actual_size, i;

         actual_size = array_from_file (array, 100);

         for (i=0; i < actual_size; ++i)
                printf ("%3.1lf ", array[i]);

         printf   ("\nThe   array   contains   %d   values   ",
actual_size);
         printf ("for a capacity of 100 cells.\n");

         return (0);
}
```


43.3 56.1 23.4 87.5 123.2 13.4 77.1
The array contains 7 values for a capacity of 100 cells.

Example 16: Add the corresponding values from two arrays of the same size.

```
#include <stdio.h>
```

```
/* the function that adds the two arrays a1 and a2. it "returns"
a3 back */
void
addarrays (int a1[], int a2[], int a3[], int n)
{
      int i;

      /* do the adding of every corresponding cells */
      for (i=0; i<n; ++i)
            a3[i] = a1[i] + a2[i];
}

int
main (void)
{
      int x[] = {1,2,3,4}, i;
      int y[] = {10,20,30,40};
      int z[4];

      /* call the function */
      addarrays (x, y, z, 4);

      /* print a report */
      for (i=0; i<4; ++i)
            printf ("%3d", x[i]);

      printf ("\n + \n");

      for (i=0; i<4; ++i)
            printf ("%3d", y[i]);

      printf ("\n-------------\n");

      for (i=0; i<4; ++i)
            printf ("%3d", z[i]);

      return (0);
}
```



```
 1 2 3 4
+
10 20 30 40
-------------
11 22 33 44
```

Example 17: The Basic Search Algorithm for A 1-D Array .

```
#include <stdio.h>

int
search (int arraytosearch[], int valuetosearch, int size)
{
```

```
      int i, found;

      /* initialize found at -1, if value not found, stays at -1
*/
      found = -1;

      /* search until found or until end of array */
      i = 0;
      while (found<0 && i<size)
      {
            if (arraytosearch[i] == valuetosearch)
                  found = i; /* I have found it! */
            else
                  i = i + 1;
      }
      return (found);
}


int
main (void)
{

      int x[] = {12,67,56,60,88,34,123};
      int value = 60;
      int pos, i;

      pos = search (x, value, 7);

      if (pos >= 0)
            printf ("%d was found at position %d.\n", value,
pos);
      else
            printf ("%d was not found in the array.\n",
value);


      return (0);
}
```


60 was found at position 3.

Example 18: A dynamically-allocated 1-D array .

```
#include <stdio.h>

int main (void)
{

      double* array; /* declare a pointer only */
      int i, size;

      /* ask user for size of array */
      printf ("How large do you want your array? ");
```

```
        scanf ("%d", &size);

        /* allocate the array in the heap */
        array = (double *) calloc (size, sizeof(double));

        /* printing the array for verification
        surprise! a dynamic array is
        automatically initialized with zeros! */
        for (i = 0; i < size; ++i)
             printf ("%6.2lf", array[i]);

        /* freeing the memory allocation */
        free (array);

        return (0);
}
```

How large do you want your array? 7
0.00 0.00 0.00 0.00 0.00 0.00 0.00

Example 19: Searching for a value inside 2-D Array .


```
#include <stdio.h>
#define MAXSIZE 100

int
search2d (int array[][MAXSIZE], int value, int size, int
*foundcol)
{
     /* foundrow will return the row where the value was found
          or -1 if value not found */
     /* *foundcol will be returning the column where the value
          was found. It remains undefined if not found */

     int i, j, foundrow;

     /* initialize found at -1, if value not found, stays -1 */
     foundrow = -1;

     /* search until found or until end of array */
     for (i=0; i<size; ++i)
          for (j=0; j<size; ++j)
          {
               if (array[i][j] == value)
               {
                    foundrow = i; /* I have found it! */
                    *foundcol = j;
               }
          }
     return (foundrow);
}
```

```
int
main (void)
{

   int x[100][100], value, row, col, size, i, j;

   value = 99; /* the value I am searching */

   /* reading size from file */
   scanf ("%d", &size);

   /* fills array from file using redirection */
   for (i=0; i<size; ++i)
      for (j=0; j<size; ++j)
         scanf ("%d", &x[i][j]);

   /* calling the search function */
   row = search2d (x, value, size, &col);

   if (row >= 0)
      printf ("%d found at row %d / column %d.\n", value,
row, col);
   else
      printf ("%d not found in the array.\n", value);

   return (0);
}
```


99 was found at row 3 / column 1.

Example 20: Scalar Product of Two Vectors .

```
#include <stdio.h>

int main (void)
{
     int scalar_product, n, k;
     int v1[]={2,3,1};
     int v2[]={1,2,4};

     scalar_product = 0;
     n=3;


     for (k=0; k<n; ++k)
          scalar_product = scalar_product + v1[k]*v2[k];

     printf ("The scalar product is: %d.", scalar_product);

     return (0);
}
```

The scalar product is: 12.

Example 21: Multiplication of a matrix by a vector.

```
#include <stdio.h>

#define COLS 3
#define ROWS 4

int
main (void)
{
     int i,k;
     int vec[3]={1,2,2};
     int mat[4][3]={{1,1,1},{2,3,1},{1,-1,-1},{0,1,2}};
     int prod[4];

     /* do the multiplication */
     for (i=0; i<ROWS; ++i)
     {
          prod[i] = 0;
          for (k=0; k<COLS; ++k)
               prod[i] = prod[i] + mat[i][k] * vec[k];
     }

     /* display product vector */
     printf ("The product is: <");
     for (i=0; i<ROWS; ++i)
          printf ("%d, ", prod[i]);
     printf (">\n");


     return (0);
}
```


The product is: <5, 10, -3, 6, >

Example 22: Multiplication of two matrices.

```
#include <stdio.h>

#define M 3 /* n of rows in first matrix */
#define N 4 /* n of cols in first and of rows in 2nd */
#define P 5 /* n of cols on 2nd matrix */

void
multmatrix (int a[M][N], int b[N][P], int c[M][P])
{
   int i,j,k;

   for (i=0; i<M; ++i)
      for (j=0; j<P; ++j)
      {
         c[i][j]=0.0;
         for (k=0; k<N; ++k)
            c[i][j] = c[i][j] + a[i][k] * b[k][j];
      }
}


int
main (void)
{
int i,j;
int mat1[M][N]={{1,2,2,2},{2,-3,6,4},{8,1,0,-3}};
int                    mat2[N][P]={{1,1,1,0,3},{2,3,1,6,2},{1,-1,-
1,8,3},{0,1,2,3,4}};
int matprod[M][P];

/* do the multiplication */
multmatrix (mat1, mat2, matprod);

/* display the resulting matrix */
for (i=0; i<M; ++i)
{
   for (j=0; j<P; ++j)
      printf ("%4d  ", matprod[i][j]);
   printf ("\n");
}

return (0);
}
```



```
 7   7   5  34  21
 2  -9   1  42  34
10   8   3  -3  14
```

Example 23: Dynamic allocation of a 2D array (Software Engineer's Method) .

```
#include <stdio.h>
```

```
#include <stdlib.h>

/* Dynamic allocation of arrays of more than one dimension
is easily done. You can simulate a two-dimensional
array with a single, dynamically-allocated one-dimensional
array. However, you must now perform subscript calculations
manually, accessing the [i][j]th element with
array[i * ncolumns + j]. Software engineers prefer this method
for its elegance and efficiency */

int
main (void)
{
     int nrows, ncols, i, j;
     int *numbers; /* pointer to the first cell ([0]) */

     printf ("How many rows and columns?> ");
     scanf ("%d%d", &nrows, &ncols);

     /* allocating the array of integers */
     numbers = (int *) calloc (nrows*ncols, sizeof(int));

     i=1; j=1;
     numbers[i*ncols+j] = 9; /* initializes one value to 9 */


     for (i=0; i<nrows; i=i+1)
     {
          for (j=0; j<ncols; j=j+1)
          {
               printf ("%3d ", numbers[i*ncols+j]);

          }
          printf ("\n");
     }


     free (numbers);
     return (0);
}
```



```
How many rows and columns?> 3 12
  0  0  0  0  0  0  0  0  0  0  0  0
  0  9  0  0  0  0  0  0  0  0  0  0
  0  0  0  0  0  0  0  0  0  0  0  0
```

Example 24: Dynamic allocation of a 2D array (Computer Scientist's Method).

```
#include <stdio.h>
#include <stdlib.h>

/* Dynamic allocation of arrays of more than one dimension
can also be done using a pointer pointing to an array of
```

```
pointer and each pointer of that array pointing to an array
of values. With that method you can use the real 2-D
subscripts like array[i][j] */

int
main (void)
{
     int nrows, ncols, i, j;
     int **numbers; /* pointer to the first cell ([0][0]) */

     printf ("How many rows and columns?> ");
     scanf ("%d%d", &nrows, &ncols);

     /* allocating the array of pointers */
     numbers = (int **) calloc (nrows, sizeof(int *));

     /* allocating the array of integers */
     for (i=0; i<nrows; ++i)
          numbers[i] = (int *) calloc (ncols, sizeof(int));

     i=1; j=1;
     numbers[i][j] = 9; /* initializes one value to 9 */


     for (i=0; i<nrows; i=i+1)
     {
          for (j=0; j<ncols; j=j+1)
          {
               printf ("%3d ", numbers[i][j]);

          }
          printf ("\n");
     }

     /* freeing the array */
     for (i=0; i<nrows; ++i)
          free (numbers[i]);

     free (numbers);

     return (0);
}
```



```
How many rows and columns?> 4 9
 0  0  0  0  0  0  0  0  0
 0  9  0  0  0  0  0  0  0
 0  0  0  0  0  0  0  0  0
 0  0  0  0  0  0  0  0  0
```

13.2 FUNCTIONS:

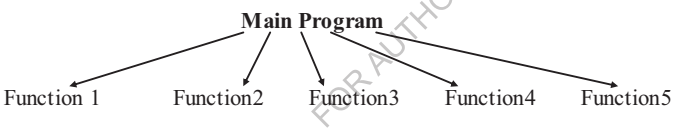
13.2.1 NEED FOR USER-DEFINED FUNCTIONS:

The function main() is a specially recognized function in C. Every program must have a main function to indicate where the program has to begin its execution. It is possible to code any program utilizing only main function, it leads to a number of problems. The program may become too large and complex and as a result the task of debugging, testing and maintaining becomes difficult. If a program is divided into functional parts, then each part may be independently coded and later combined into a single unit. These subprograms called 'functions' are much easier to understand, debug, and test. Sometimes it is also called "divide and conquer ".

There are times when some type of operation or calculation is repeated at many points throughout a program. In such situations, we may repeat the program statements wherever they are needed. There is another way to design a function that can be called and used whenever required. This saves both time and space.

This approach clearly results in a number of advantages.

1. The figure below shows to-down modular programming. In this programming style, the high level logic of the overall problem is solved first while the details of each lower-level function are addressed later.
2. The length of a source program can be reduced by using functions at appropriate places.
3. It is easy to locate and isolate a faulty function for further investigations.
4. A function may be used by many other programs.



Top-down modular programming using functions

13.2.2 DEFINING AND USING FUNCTIONS:

All the functions have the form:

```
Function-name(argument list)
{
     local variable declarations;
     executable statement1;
     executable statement2;
     ---------------------------;
     ---------------------------   ;
     return(expression);
}
```

All parts are not essential. Some may be absent. For example, the argument list and its associated argument declaration parts are optional. The declaration of local variables is required only when any local variables are used in the function. A function can have any

number of executable statements. A function that does nothing, may not include any executable statements at all.

```
Do_nothing() {}
```

The return statement is the mechanism for returning a value to the calling function. This is also optional statement. Its absence indicates that no value is being returned to the calling function.

Function name:

A function must follow the same rules of formation as other variable names in C.

Argument List:

The argument list contains valid variable names separated by commas. The list must be surrounded by parentheses. The argument variables receive values from the calling function, thus providing a means for data communication from the calling function to the called function. Some examples of functions with arguments are:

```
Quadratic(a,b,c)
          Power(x,n)
          Mul(a,b)
```

All the argument variables must be declared for their types after the function header and before the opening brace of the function body.

```
Power(x,n)
float x;
int n;
{
   ---------
   ---------
    ---------
}
```


13.2.3 CATEGORY OF FUNCTIONS:

A function may depend on whether arguments are present or not and whether a value is returned or not. It may belong to one of the following categories.

Category 1: Functions with no arguments and no return values.
Category 2: Functions with arguments and no return values.
Category 3: Functions with arguments and return values.

Category 1: No arguments and no return values:

When a function has no arguments, it does not receive any data from the calling function. Similarly, when it does not return a value, the calling function does not receive any data from the called function. In effect, there is not data transfer between the calling function and the called function. The dotted lines indicate that there is only a transfer of control but not data.

```
Function1()          No input        function2()

{                                      {
 ----------------
function2()                              ----------
 ----------------                        ----------
 ----------------                        ----------
            }                          }
```

A program with three user-defined functions is given below.

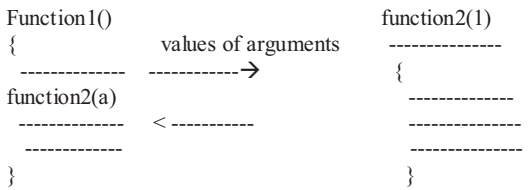
Category 2: Functions with no arguments, no return values:

```
main()
     {
        printtext();
         value();
         printtext();
  }
printtext()
{
     int I;
     for (i=1;i<=40;i++)
       printf("%c", '-');
       printf("\n");
}

value()
{
     int year, period;
      float inrate, sum principal;
      printf("Principal amount?");
     scanf("%f", &principal);
     printf("Interest rate?   ");
     scanf("%f", &inrate);
     printf("Period?             ");
      scanf("%d",   &period);
        sum=principal;
         year=1;
        while(year<=period)
        {
          sum=sum * (1+inrate);
          year=year+1;
         }
printf("    \n    8.2f    %5.2f           %5d       %12.2f\n",
principal,inrate,period,sum);
}
```

Category 1: Functions with arguments and no return values:

We can make the calling function to read data from the terminal and pass it on to the called function. The nature of data communication between the calling function and the called function with arguments but no return values is shown below.



For example.

```
Printtext(ch)
Value(p,r,n)
```

The arguments ch,p,r and n are called the formal arguments. The calling function can now send values to these arguments using function calls containing appropriate arguments. For example, the function call

```
Value(100,0.23,10)
```

Would send the values 100,0.23,and 10 to the function.

```
Value(p,r,n)
```

And assign 100 to p, 0.23 ,to r, and 10 n. The values 100,0.23 and 10 are the actual arguments which become the values of the formal arguments inside the called function.

The actual and formal functions should match in number, type and order. The values of actual arguments are assigned to the formal arguments on a one to one basis starting with the first argument.


```
          main()
          {
Function
call          ---------------
-----→        function1(a1,a2,a3.....am)
              -------------
          }
Called function
------ >              function1(f1,f2,f3,.....fn)
                 ---------------
                 ---------------
                 {
                ----------
                        ----------
                   }
```

The formal arguments must be valid variable names, the actual arguments may be variable names, expressions or constants. The variables used in actual arguments must be assigned values before the function call is made.

When a function call is made, only a copy of the values of actual arguments is passed into the called function.

The function call `value(prin, rate, per);`

Passes information it contains to the function value.

The function header of value has three formal arguments p,r and n which correspond to the actual arguments in the function call, namely, prin,rate and per. The formal arguments are declared immediately after the function header. On execution of the function call, the values of the actual arguments are assigned to the corresponding formal arguments.

```
p=prin;
r=rate;
n=per;
```

The variable declared inside a function are known as local variables and therefore their values are local to the function and cannot be accessed by any other function.

The function value calculates the final amount for a given period and prints the result. Control is transferred back on reaching the closing brace of the function. Note that the function does not return any value.

Example 25: Program to show functions with arguments but no return values

```
main()
  {
     float prin.rate,amt;
     int per;
     printf("Enter principal amount, interest");
     printf("rate and period\n");
     scanf("%f %f %d", &prin,&rate,&per);
             printtext('Z');
     value(prin,rate,per);
     printtext('A');
}

   printtext(ch)
   char ch;
{
     int j;
     for(j=1;j<=52;j++)
      printf("%c", ch);
       printf("\n");
}
     value(p,r,n)
      int n;
       float p,r;
        {
           int year;
```

```
            float sum;
             sum=p;
            year=1;
            while(year<=n)
          {
             sum=sum*(1+r)
                    year=year+1;
          }
     printf("%f %f %d  %f \n", p, r, n, sum);
}
```

Arguments with return values:

We may not always wish to have the result of a function displayed. We may use it in the calling function for further processing. Moreover , to assure a high degree or portability between programs, function should generally be coded without involving any I/O operations. Different programs may require different output
Formats for displaying results. This can be overcome by handing over the result of a function to its calling function where the returned value can be required by the program.

Example 26: Program to show functions with arguments and return values.


```
     main()
       {
          float prin.rate,amt;
          int per;
          printf("Enter principal amount, interest");
          printf("rate and period\n");
          scanf("%f %f %d", &prin,&rate,&per);
               printtext('*', 52);
              amt=value(prin,rate,per);
          printf("\n    %f    %f    %d    %f    \    n    \n",
prin,rate,per,amt);
          printtext('=', 52);
     }

        printtext(ch,l)
        int l;
        char ch;
     {
          int j;
          for(j=1;j<=52;j++)
           printf("%c", ch);
            printf("\n");
}

     value(p,r,n)
      int n;
       float p,r;
        {
           int year;
            float sum;
             sum=p;
```

```
        year=1;
        while(year<=n)
      {
         sum=sum*(1+r)
                year=year+1;
      }
            return(sum);
}
```

1. The function call transfers the control along with the copies of the values of the actual arguments to the function value where the formal arguments p,r and n are assigned the values of prin, rate and per respectively.
2. The called function value is executed line by line in a normal fashion until the return (sum); statement is encountered. The value of sum is passed back to the function call in the main program.
3. The calling statement is executed normally and the returned value is thus assigned to amt.

Returning non-integer value from functions:

The function value mentioned above in the example does all the calculations using floats but the return statement

```
return(sum);
```

returns only the integer part of sum. This is due to the absence of the type-specifier in the function header. Some times it might be necessary to receive float or double type of data.

We should follow the steps below to enable a calling function to receive a non-integer value from a called function.

1. The explicit type_specifier, corresponding to the data type required must be mentioned in the function header. The general form of the function definition is.

```
Type-specifier function-name(argument list)
     argument declaration;
     {
         function statements;
     }
```

The type-specifier tells the compiler, the type of data the function is to return.

2. The called function must be declared at the start of the body in the calling function like any other variable. This is to tell the calling function the type of data that the function is actually returning.

Example 27: Program showing the transfer of a floating-point value between functions.

```
main()
  {
  float x,y, mul();
  double div();
  x= 34.238;
        y= 6.78;
  printf("%f \n", mul(x,y));
  printf("%f \n", div(x,y));
      }
  float mul(x,y)
```

```
float x,y;
{
   return(x * y);
}

double div(p,q)
double p,q;
{
     return(p/q);
      }
}
```

The declaration part of main function declares not only the variables but the functions mul and div as well. This only tells the compiler that mul will return a float-type value and div a double type value. Parantheses that follow mul and div specify that they are functions instead of variables.

If we have a mismatch between the type of data that the called function returns and the type of data that the calling function expects, we will have unpredictable results. We must be very careful to make sure that both types are compatible.

13.2.4 ARRAY IN FUNCTIONS.

It is possible to pass the values of an array to a function. To pass an array to a called function, it is sufficient to list the name of the array without any subscripts, and the size of the array as arguments.

The largest(a,n):

Will pass all the elements contained in the array a of size n. The called function expecting this call must be defined appropriately. The largest function header might look like:

```
float largest(array,size)
float array[ ];
int size;
```

The function largest is defined to take arguments , the array name and the size of the array to specify the number of elements in the array. The declaration of the formal argument array is made as follows:

```
float array[ ];
```

The pair of brackets informs the compiler that the argument is an array of numbers. It is not necessary to specify the size of the array here.

Consider the following example:

```
main()
{
   float large();
    static        float        value[5]={        3.4,-
12.78,1.23,5.67,8.90};
   printf("%f \n", large(value,5));
}
    float large(x,n)
     float a[ ];
     int n;
     {
```

```
            int j;
                    float max;
                    max=a[0];
            for(j=1; j<n; j++)
               if(max< a[j])
                  max=a[j];
                       return(max);
}
```

When the function call large(value,5) is made the value of all elements of the array value are passed to the corresponding elements of array a in the called function. The large function finds the largest value in the array and returns the result to the main.

Global variables:

Variables that are both alive and active throughout the entire program are known as global or external variables. The global variables can be accessed by any function in the program. External variables are declared outside a function.

The external declaration of integer number and float length might appear as:

```
            int number;
            float length=7.5;
            main()
            {
                      ----------
               ---------
                           }

      function1()
      {
         ------------
         ----------
      }

      function2()
      {
        ---------
         --------
      }
```


The variables number and length are available for use in all the three functions. When the local variable and a global variable have the same name, the local variable will have precedence over the global one in the function where it is declared.

Consider the following example:

```
            int cnt;
            main()
            {
               cnt=10;
                ------------
                -----------
                          }
                           function()
               {
```

```
                int cnt=0;
                 ----------
                 ----------
          cnt=cnt+1;
                          }
```

When the function references the variable cnt, it will be referencing only its local variable, not the global one. The value of cnt in main will not be affected.

Example 28: A program to show the properties of global variables.

```
int x;
main()
{
     x=15;
     printf("x= %d \n", x);
     printf("x=%d \n", fun1());
     printf("x=%d\n", fun2());
     printf("x=%d\n", fun3());
}
fun1()
{
     x=x+15;
     return(x);
}

fun2()
{
     int x;
     x=1;
     return(x);
}
fun3()
{
     x=x+15;
     return(x);
}
```


Local variables:

These type of variables are declared inside a function in which they are to be utilized. They are created when the function is called and destroyed automatically when the function is exited. Hence these variables are also known as automatic variables.

A variable declared inside a function without storage class specification is by default a local variable.

```
main()
{
     int number;
      ------------
      ------------
}
```

Example 29: Program to show the working of local variables.

```
main()
{
     int m=1000;
     function2();
     printf("%d\n", m);
}

function1()
{
     int m=10;
     printf("%d\n", m);
}

function2()
{
     int m=1000
     function();
     printf("%d\n", m);
}
```

Register variable:

Some times we can tell the compiler that a variable should be kept in one of the machine's registers, instead of keeping in the memory. Since the access of register variables is faster than the memory access. The general format is as follows:

Register int variable name;

Since only a few variables can be placed in the register, it is important to carefully select the variables for this purpose. Once the limit is reached C will automatically convert register variables into non-register variables.

Static variable:

A variable can be declared static using the keyword static like

```
static int a;
static float y;
```

A static variable may be either an internal type or external type, depending on the place of declaration.

Internal static variables are those which are declared inside a function. The scope of internal static variables extend up to the end of the function in which they are defined. These internal static variables are similar to local variables except that they remain in existence throughout the remainder of the program. Therefore , internal static variables can be used to retain values between function calls.

Example 30: Program to show static variable

```
main()
{
     int j;
```

```
      for(j=1;j<=3;j++)
      stat();
}

      stat()
{
      static int y=0;
      y=y+1;
      printf("y=%d \n",y);
}
```

Example 31: Program to calculate standard deviation using function.

```
#include<math.h>
main()
{
      float value[5], stddev();
      int i;
      printf("Enter the values\n");
      for(i=0;i<5;i++)
      scanf("%f", &value[i]);
      printf("Std.deviation is %f\n", stddev(value,5);
}
float stddev(x,n)
float x[ ];
int n;
{
      int i;
      float mean(),y,sum=0.0;
      y=mean(x,n);
      for(i=0;i<n;i++)
      {
            sum=sum+(y-x[i])*(y-x[i]);
            return(sqrt(sum/(float)n));
        }
float mean(x,n)
float x[ ];
int n;
{
int i;
float sum=0.0;
for(i=0;i<n;i++)
  sum=sum+x[i];
return(sum/(float)n);
}
```


Example 32: Program to show sorting of array elements.

```
      Main()
      {
            int i;
            static int num[6]={34,56,23,12,95,67};
            printf("The numbers before soring\n:");
```

```
            for(i=0;i<6;i++)
                printf(i=0;i<6;i++)
                 printf("\n");
}
sort(n,y)
int m, x[ ];
{
     int i,j,temp;
     for(i=1   ; i<=n;i++)
        for(j=1;j<=n-i;j++)
            if(x[j-1]>=x[j])
          {
              temp=x[j-1];
               x[j-1]=x[j];
                x[j]=temp;
   }
 }
```

Example 33: A user-defined function without argument nor result

```
#include <stdio.h>

/* the function definition */
void
stars (void)
{
   printf ("*******************************\n");
}
/* end of function definition */


/* main program */
int
main (void)
{
   printf ("The line of stars comes from a function.\n");

   /* calling the function */
   stars ();

   /* the function can be called as will*/
   printf ("\n");
   stars ();
   printf ("Hello world!\n");
   stars ();

   return (0);
}
```


The line of stars comes from a function.
****

****

```
Hello world!
******************************
```

Example 34: A void function with one argument.

```
#include <stdio.h>

/* a void function returns nothing */
void
stars2 (int n)
{
      int i;

      /* a loop displaying a star at
      each iteration */
      for (i=1; i<=n; ++i)
      {
            printf ("*");
      }
      /* change line after each series */
      printf ("\n");
}

int
main (void)
{
      int a;

      a=10;

      /* the argument may be a constant,
      a variable or an expression */

      stars2 (20);
      stars2 (a);
      stars2 (a+2);

      return (0);
}
```



```
********************
**********
************
```

Example 35: A function with a prototype.

```
/* You can put only the prototype (header) on top */
/* and define the function at the bottom */
#include <stdio.h>

/* the function prototype */
void stars2 (int n);

/* the main program */
int
```

```
main (void)
{
      int a;

      a=10;

      /* the argument may be a constant,
      a variable or an expression */

      stars2 (20);
      stars2 (a);
      stars2 (a+2);

      return (0);
}

/* the function definition */
void
stars2 (int n)
{
      int i;

      /* a loop displaying a star at
      each iteration */
      for (i=1; i<=n; ++i)
      {
            printf ("*");
      }
      /* change line after each series */
      printf ("\n");
}
```



```
********************
**********
************
```

Example 36: The factorial function: one argument, one result .

```
#include <stdio.h>

/* this function will return an integer */
int
factorial (int n)
{
      int i, product;

      product = 1; /* initialization */

      /* computes n*n-1... */
      for (i=n; i>1; i=i-1)
      {
            product = product * i;
      }

      /* the value that goes out */
      return (product);
```

```
}


int
main (void)
{
      int a, result;

      printf ("Enter an integer number: ");
      scanf ("%d", &a);

      /* calling the function */
      result = factorial (a);

      /* printing the report */
      printf ("The factorial of %d is %d.\n", a, result);

      return (0);
}
```

/* NOTE: a large number will produce an arithmetic overflow */

Enter an integer number: 13
The factorial of 13 is 1932053504.

Example 37: The bigger function: two arguments, one result .

```
#include <stdio.h>

/* a function taking two double numbers and returning
the larger number of the two */

/* this function will return a double */
double
bigger (double n1, double n2)
{
      double big;

      if (n1>n2)
            big = n1;
      else
            big = n2;

      return (big);
}


int
main (void)
{
      double x, y, result;

      printf ("Enter a real number: ");
      scanf ("%lf", &x);
```

```
        printf ("Enter a real number: ");
        scanf ("%lf", &y);

        /* calling the function (2 arguments) */
        result = bigger (x,y);

        /* printing the report */
        printf ("The bigger number is %lf.\n", result);

        return (0);
}
```

Enter a real number: 12.4
Enter a real number: 67.3
The bigger number is 67.300000.

Example 38: Function finding prime numbers (no pointers) .

```
#include <stdio.h>
#include <math.h>

/* function returns true if n is even.  */
/* it returns false if n is odd         */
int
even (int n)
{
        return (n%2==0);
}


/* function returns true if n is prime */
int
prime (int n)
{
        int divisor, i;

        /* looking for a divisor. if found, it
                is not a prime number */

        divisor = 0;

        /* eliminating even numbers except 2 */
        if (even (n))
        {
                if (n == 2)
                        divisor = 0;
                else
                        divisor = 2;
        }
        else
        {
                if (n == 1)
                        divisor = 0; /* 1 is a prime number */
                else
                        /* trying to divide number by 3,5,7,... */
```

```
                /* to find a divisor until we reach n-1      */
                for (i = 3; i < n; i = i + 2)
                {
                     if (n % i == 0)
                          divisor = i;
                }
        }

        /* if there is a divisor (not zero) then NOT prime */
        return (!divisor);
}


int
main (void)
{
        int x;

        printf ("Enter a positive integer number: ");
        scanf ("%d", &x);

        /*  testing for prime and printing the report */
        if (prime (x))
             printf ("%d is a prime number.\n", x);
        else
             printf ("%d is not a prime number.\n", x);

        return (0);
}
```


Enter a positive integer number: 59
59 is a prime number.

Example 39: Write a program that prints out all the prime numbers between 1 and 1000.

```
#include <stdio.h>
#include <math.h>

/* function returns true if n is even.  */
/* it returns false if n is odd         */
int
even (int n)
{
        return (!(n%2));
}


/* function returns true if n is prime */
int
prime3 (int n)
{

        int divisor, i;
        /* looking for a divisor. if found, it
             is not a prime number */
```

```
        divisor = 0;

        /* eliminating even numbers except 2 */
        if (even (n))
        {
              if (n==2)
                    divisor=0;
              else
                    divisor=1;
        }
        else
        {
              if (n==1)
                    divisor=0; /* 1 is a prime number */
              else
                    /* trying to divide number by 3,5,7,... */
                    /* to find a divisor until sqrt(n)      */
                    for (i=3; i<=sqrt(n); i=i+2)
                    {
                          if (!(n%i))
                                divisor=i;
                    }
        }

        /* if there is a divisor then NOT prime */
        return (!divisor);

}
```


Example 40: This main program prints all prime numbers between 1 and 1000

```
int
main (void)
{
      int x;

      for (x=1; x<=1000; ++x)
            if (prime3 (x))
                  printf (" %d ", x);


      return (0);
}
```

Example 41: This program shows a function that generates two results. One result is returned (-), the other accessed from the main via an address (+).

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

```
#include <stdio.h>
#include <math.h>

double
quadratic (int a, int b, int c, double* xplus)
{
      double xminus;

      xminus  = (-b - sqrt (b * b - 4 * a * c))/ (2 * a);
      *xplus  = (-b + sqrt (b * b - 4 * a * c))/ (2 * a);
      return (xminus);
}


int
main (void)
{
      int a = 10, b = 40, c = 30;
      double xplus, xminus;

      /* calling the function. the address of xplus is sent as an
argument */
      xminus = quadratic (a, b, c, &xplus);

      printf ("Using +: %lf\n", xplus);
      printf ("Using -: %lf\n", xminus);

      return (0);
}
```


Using +: -1.000000
Using -: -3.000000

Example 42: Write a void function that "returns" the largest value of two real numbers.

```
/* this function returns nothing but will
change the value of the variable in the calling
function's memory area */

void
bigger2 (double n1, double n2, double *result)
{

      if (n1>n2)
            *result = n1;
      else
```

```
            *result = n2;

/* *result in bigger2 uses the same
memory cell as result in main */
}



int
main (void)
{
      double x, y, result;

      printf ("Enter a real number: ");
      scanf ("%lf", &x);

      printf ("Enter a real number: ");
      scanf ("%lf", &y);

      /* calling the function (3 arguments) */
      /* &result is the address where variable result is stored
*/
      bigger2 (x, y, &result);

      /* printing the report */
      printf ("The largest number is %f.\n", result);

      return (0);
}
```



```
Enter a real number: 12.4
Enter a real number: 67.3
The largest number is 67.300000.
```

Example 43: Write a function that determines if a number is prime or not. The function must return 1 if prime, 0 if not. In addition, the function must "return" the value of one of the divisors.

```
#include <stdio.h>
#include <math.h>

/* function returns true if n is even.  */
/* it returns false if n is odd         */
int
even (int n)
{
      return (!(n%2));
}


/* function returns true if n is prime,
the pointer variable references the divisor value */
int
prime2 (int n, int *divisor)
```

```
{
      int i, is_prime;

      /* looking for a divisor. if found, it
            is not a prime number */
      *divisor = 0;

      /* eliminating even numbers except 2 */
      if (even (n))
      {
            if (n==2)
                  *divisor=0;
            else
                  *divisor=2;
      }
      else
      {
            if (n==1)
                  *divisor=0; /* 1 is a prime number */
            else
                  /* trying to divide number by 3,5,7,... */
                  /* to find a divisor until sqrt(n)      */
                  for (i=3; i<=sqrt(n); i=i+2)
                  {
                        if (!(n%i))
                              *divisor=i;
                  }
      }

      is_prime = *divisor;

      /* if there is a divisor then NOT prime */

      return (!is_prime);
}

int
main (void)
{
int x, div;

   printf ("Enter a positive integer number: ");
   scanf ("%d", &x);

   /*  testing for prime and printing the report */
   if (prime2 (x, &div))
      printf ("%d is a prime number.\n", x);
   else
      printf ("%d not prime number. Divisible by %d.\n", x,
div);

return (0);
}
```


Enter a positive integer number: 77
77 not prime number. Divisible by 7.

Example 44: Write a function that takes in an integer number and"returns" both twice the number and three times the number.

```
#include <stdio.h>

/* double_triple function begins */
int
double_triple (int x, int *d)
{
      int t;
      *d=2*x; /* double "returned" via pointer */
      t=3*x;
      return (t); /* triple returned the standard way */
}
/* double_triple function ends */



/* main program begins */
int
main(void)
{

      int a,twice,thrice;
      a=10;
      thrice = double_triple (a, &twice);
      printf("%d is two times %d.\n",twice,a);
      printf("%d is three times %d.\n",thrice,a);

      return(0);
}
/* main program ends */
```


20 is two times 10.
30 is three times 10.

Example 45: This function takes a real number and separates it into three parts: a sign (a character value), a whole part (an integer) and a fraction (double).

```
#include <stdio.h>
#include <math.h>

/* the function returns the sign but the pointer parameters */
/* will modifiy the corresponding variable arguments in    */
/* main program                                             */

char
separate (double number, int *w, double *f)
{
```

```
      char s;
      double magnitude;  /* the absolute value of the number */

      /* testing if positive or negative and assignation of sign
*/
      if (number < 0)
            s = '-';
      else  if (number == 0)
                        s = ' ';
                  else
                        s = '+';

      magnitude = fabs (number);
      *w = floor (magnitude);
      *f = magnitude - *w;
      return (s);
}


int
main (void)
{
      double n; /* the original number */

      /* the variables that will be filled by the function */
      char sign;
      int whole;
      double fraction;

      printf ("Enter a real number: ");
      scanf ("%lf", &n);

      /* calling the function */
      sign = separate (n, &whole, &fraction);

      /* printing the report */
      printf ("Parts of %f: \n", n);
      printf ("===============\n\n");
      printf ("Sign is: %c \n", sign);
      printf ("Whole part is %d \n", whole);
      printf ("Fraction part is %f \n", fraction);

      return (0);
}
```



```
Enter a real number: -46.73
Parts of -46.730000:
============

Sign is: -
Whole part is 46
Fraction part is 0.730000
```

Example 46: This is simple addition reader/parser for 2 doubles.

```
#include <stdio.h>

/* function to read expression */
void
readex (double *op1, double *op2)
{
      char plus;
      /* no & required in scanf because &*op1 is the same thing
as op1  */
      scanf ("%lf %c %lf", op1, &plus, op2);
}



int
main(void)
{

      double a, b, c;
      printf ("Enter an addition expression (eg: 4.5+3.5):
");
         /* the addresses of the two operands are sent to the
function  */
      readex (&a, &b);
      c = a + b;
      printf("%lf + %lf is %lf.\n",a,b,c);

      return(0);
}
/* can you expand this program to cover substractions? */
```


Enter an addition expression (eg: 4.5+3.5): 13.4+5.6
13.400000 + 5.600000 is 19.000000.

Example 47: Write a function that multiplies two integerswithout using the multiplication (*) operator.

```
#include <stdio.h>
int multiply (int m, int n)
{
      int answer;
      if (n == 1)
            answer = m;
      else
            answer = m + multiply (m, n-1);

      return (answer);
}


int
```

```
main (void)
{

     int a, b, c;
     a = 20;
     b = 10;
     c = multiply (a, b);
     printf("%d times %d is %d. \n", a, b, c);

     return(0);
}
```

20 times 10 is 200.

Example 48: Functions from the math library.

```
#include <stdio.h>
#include <math.h>
#define PI 3.1416

int
main (void)
{
   double before, after, x, y, z;

   /* the ceil function */
   before = -217.5;
   after = ceil (before);
   printf ("The ceiling of %3.1lf is %3.1lf\n", before,
after);

   /* the floor function */
   before = -217.5;
   after = floor (before);
   printf ("The floor of %3.1lf is %3.1lf\n", before,
after);

   /* the log function */
   before = 200.0;
   after = log (before);
   printf ("The ln of %3.1lf is %3.1lf\n", before, after);

   /* the log10 function*/
   before = 200.0;
   after = log10 (before);
   printf ("The log of %3.1lf is %3.1lf\n", before, after);

   /* the sqrt function*/
   before = 200.0;
   after = sqrt (before);
   printf ("The square root of %3.1lf is %3.1lf\n", before,
after);
```

```
   /* the fabs function (for doubles)*/
   before = -413.56;
   after = fabs (before);
   printf ("The absolute value of %3.1lf is %3.1lf\n",
before, after);

   /* the sin function */
   before = 45.0;
   after = sin (before * PI / 180);
   printf ("The sine of %3.1lf is %5.3lf\n", before,
after);

   /* the cos function */
   before = 45.0;
   after = cos (before * PI / 180);
   printf ("The cosine of %3.1lf is %5.3lf\n", before,
after);

   /* the tan function */
   before = 45.0;
   after = tan (before * PI / 180);
   printf ("The tangent of %3.1lf is %5.3lf\n", before,
after);

   /* the exp function */
   before = 10.0;
   after = exp (before);
   printf ("e to the power of %3.1lf is %5.3lf\n", before,
after);

   /* the pow function */
   x = 9.0; y = 3.0;
   z = pow (x, y);
   printf ("%3.1lf to the power of %3.1lf is %3.1lf\n", x,
y, z);

   return (0);
}
```


The ceiling of -217.5 is -217.0
The floor of -217.5 is -218.0
The ln of 200.0 is 5.3
The log of 200.0 is 2.3
The square root of 200.0 is 14.1
The absolute value of -413.6 is 413.6
The sine of 45.0 is 0.707
The cosine of 45.0 is 0.707
The tangent of 45.0 is 1.000
e to the power of 10.0 is 22026.466
9.0 to the power of 3.0 is 729.0

13.3 STRINGS

13.3.1 STRING VARIABLE:

A string is an array of characters. Any group of characters defined between double quotation marks is called a constant string.
Example:
"Good Morning Everybody"

Character strings are often used to build meaningful and readable programs.
A string variable is any valid C variable name and is always declared as an array.

13.3.2 DECLARING AND INITIALIZING STRING VARIABLES:

The general form of string variable is

```
char string_name[size];
```

The size determines the number of characters in the string-name.

Some examples are:

```
char  state[10];
char  name[30];
```

When the compiler assigns a character string to a character array, it automatically supplies a null character('\0') at the end of the string.

Character arrays may be initialized when they are declared. C permits a character array to be initialized in either of the following two forms:

```
Static char state[8]=" GUWAHATI";
Static                                                    char
state[8]={'G','U','W','A','H','A','T','I','\O'};
```

The reason that state had to be 8 elements long is that the string GUWAHATI contains 8 characters and one element space is provided for the null terminator.

C also permits us to initialize a character array without specifying the number of elements.
For example, the statement

```
     static char string[ ]    ={'H',  'E',  'L',  'L',  'O'
\O};
```

Defines the array string as a six element array.

13.3.3 READING AND WRITING STRINGS:

To read a string of characters input function scanf can be used with %s format specification.

Example:

```
char add[20];
Scanf("%s", add);
```

Note that unlike previous scanf calls, in the case of character arrays, the &(ampersand) is not required before the variable name. The scanf function automatically terminates the string that is read with a null character and therefore the character array should be large enough to hold the input string plus the null character.

Program to read a series of words using scanf function

```
main()
{
    char text1[50],text2[50],text3[50],text4[50];
    printf("Enter   text:\n");
    scanf("%s  %s", text1,text2);
    scanf("%s", text3);
    scanf("%s", text4);
    printf("\n");
    printf("text1= %s\n text2=%s\n", text1,text2);
    printf("text3=  %s\n text4= %s\n", text3,text4);
}
```

Writing strings:

The printf function with %s can be used to display an array of characters that is terminated by the null character.

Example:

```
printf("%s",  text);
```

Can be used to display the entire contents of the array name.

We can also specify the precision with which the array is displayed. For example, the specification

%12.4

indicates that the first four characters are to printed in a field width of 12 columns.

Example 49: Program to illustrate writing strings using %s format

```
Main()
{
     static char state[15]= "MADHYA PRADESH";
     printf("\n \n");
     printf("----------------------------------\n");
     printf("%13s\n", state);
     printf("%5s\n", state);
     printf("%15.6s \n", state);
     printf("%15.0s\n", state);
            printf("%.3s\n", state);
}
```

13.3.4 STRING FUNCTIONS:

C library supports a large number of string functions. The list given below depicts the string functions

Function	Action
strcat()	concatenates two strings
strcmp()	compares two strings
strcpy()	copies one string with another
strlen()	finds the length of a string.

String Concatenation :strcat() function:

The strcat function joins two strings together. The general form is

```
strcat(string1,string2);
```

string1 and string2 are character arrays. When the function strcat is executed. String2 is appended to string1. It does so by removing the null character at the end of string1 and placing string2 from there. The string at string2 remains unchanged.

Example:

Text1= VERY \0
Text2= GOOD\0
Text3= BAD\0

Strcat(text1,text2);

Text1= VERY GOOD\0
Text2= GOOD\0

Strcat(text1,text3);

Text1= VERY BAD
Text2= BAD

We must make sure that the size of string1 is large enough to accommodate the final string.
Strcat function may also append a string constant to string variable.
For example:

```
strcat(text1,"GOOD");
```

C permits nesting of strcat functions. The statement

strcat(strcat(string1,string2),string3);

Is allowed and concatenates all the three strings together. The resultant string is stored in string1.

String comparison/strcmp() function:

The strcmp function compares two strings identified by the arguments and has a value 0 if they are equal.

The general form is :

```
strcmp(string1,string2);
```

String1 and string2 may be string variables or string constants.

Examples are:

```
strcmp(name1,name2);
strcmp(name1, "ABHI");
strcmp("ROM", "RAM");
```

We have to determine whether the strings are equal, if not which is alphabetically above.

String copying/strcpy() function:

The strcpy() function works almost like a string-assignment operator. The general format is

strcpy(string1,string2);

It copies the contents of string2 to string1. string2 may be a character variable or a string constant.

For example, the statement

strcpy(city , "BANGALORE");

Will assign the string "BANGALORE" to the string variable city.

The statement strcpy(city1,city2); will assign the contents of the string variable city2 to the string variable city1. The size of the array city1 should be large enough to receive the contents of city2.

Finding the length of a string/strlen();

This function counts and returns the number of characters in a string.

The general syntax is n=strlen(string);

Where n is an integer variable which receives the value of the length of the string. The argument may be a string constant. The counting ends at the first null character.

Implementing the above functions without using string functions:

String concatenation:

We cannot assign one string to another directly,we cannot join two strings together by the simple arithmetic addition. The characters from string1 and string2 should be copied into the string3 one after the other. The size of the array string3 should be large enough to hold the total characters.

Example 50: Program to show concatenation of strings:

```
main()
{
     int i,j,k;
     static char first_name={"ABCD"};
```

```
        static char sec_name={"EFG"};
        static char  last_name={"HIJKLM"};
        char name[30];

        for(i=0;first_name[i]!='\0';i++)
             name[i]=first_name;
        for(i=0;second_name[j]!='\0'; j++)
             name[i+j+1]=sec_name[j];
                   name[i+j+1] =' ';
        for(k=0;last_name[k]!='\0';k++)
              name[i+j+k+2]=last_name[k];
              name[i+j+k+2]='\0';
               printf("\n \n");
                printf("%s \n", name);
}
```

Output

ABCD EFG HIJKLM

String comparison:

Comparison of two strings cannot be compared directly. It is therefore necessary to compare the strings to be tested, character by character. The comparison is done until there is a mismatch or one of the strings terminates into a null character.
The following segment of a program illustrates this,


```
-----------------------------
     i=0;
     while(str1[i]==str2[i] && str1[i]!='\0'
          && str2[i]!='\0')
          i=i+1;
        if(str1[i]=='\0' && str2[i]=='\0')
          printf("strings are equal\n");
           else
          printf("strings are not equal\n");
-------------------------------
```

String copying:

Example 51: Program to show copying of two strings:

```
main()
  {
     char string1[80],string2[80];
     int j;
     printf("Enter a string\n");
     printf("?");
     scanf("%s", string2);

     for(j=0;string2[i]!='\0';j++)
```

```
            string1[j]=string2[j];
            string1[j]='\0';
            printf("\n");
            printf("%s\n",string1);
            printf("Number of characters=%d\n", j);
}
```

Example 52: Program to find the length of a string:

```
#include<stdio.h>
main()
{    char line[80],character
     int c=0,i;
     printf("Enter the text\n");
     for(i=0;line[i];!='\0';i++)
{        character=getchar();
          line[i]=character;
          c++;
         }
           printf("The length of the string \n", c);
}
```

13.3.5 ARITHMETIC OPERATIONS ON CHARACTERS:

We can manipulate characters the same way we do with numbers. Whenever a character constant or character variable is used in an expression, it is automatically converted into an integer value by the system. The integer value depends on the local character set of the system.

To write a character in its integer representation , we may write it as an integer.

For example:

y='a';
printf("%d\n", y);

will display the number 97 on the screen.

It is also possible to perform arithmetic operations on the character constants and variables.

For example:

y='z'-1;

Is a valid statement. In ASCII , the value of 'z' is 122 and therefore , the statement will assign the value 121 to the variable Y.

We may also use character constants in relational expressions. For example:

ch>='a' && ch<='z'

Would test whether the character contained in the variable ch is an lower-case letter.

We can convert a character digit to its equivalent integer value using the following relationship :

y=character –'0';

Where y is defined as an integer variable and character contains the character digit.

Example: Let us assume that the character contains the digit '7', then,

y=ASCII value of '7'-ASCII value of '0'

=55-48

=7

C library has a function that converts a string of digits into their integer values. The function takes the form

y=atoi(string);

y is an integer variable and string is a character array containing a string or digits

Consider the following example:

num="1974"

year=atoi(num);

Num is a string variable which is assigned the string constant "1974". The function atoi converts the string "1974" to its numeric equivalent 1974 and assigns it to the integer variable year.

Example 53: Program to sort strings in alphabetical order:

```
#define ITEMS 10
#define MAX    25
main()
{
     char str [ITEMS][MAX], dum[MAX];
     int i=0;j=0;
           printf("Enter names of %d items \n", ITEMS);
     while(i<ITEMS)
     scanf("%s", str[i++]);

     for(i=1;i<ITEMS;i++)
{
     for(j=1;j<=ITEMS-i;j++)
      {
         if(strcmp(string[j-1],string[j])>0)
          strcpy(dummy,string[j-1]);
          strcpy(str[j-1],str[j]);
          strcpy(str[j],dummy);
     }
 }
     for(i=0;i<ITEMS;i++)
        printf("%s", str[i]);
}
```


Example 54: Program to show string handling functions:

```
#include<string.h>
main()
{
   char s1[20],s2[20],s3[20];
    int y,len1,len2,len3;
```

```
          printf("\n Enter two string constants\n");
          printf("?");
          scanf("%s %s", s1,s2);
           x=strcmp(s1,s2);
             If(y!=0)
           {
              printf("\n\n Strings are not equal\n");
               strcat(s1,s2);
           }
       else
          printf("\n\n Strings are equal\n");
          strcpy(s3,s1);
          len1=strlen(s1);
          len2=strlen(s2);
          len3=strlen(s3);
          printf("\n   s1=   %s   length=   %d   character
\n",s1,len1);
          printf("\n   s1=   %s   length=   %d   character
\n",s2,len2);
 printf("\n s1= %s length= %d character \n",s3,len3);
}
```


Example 55: Program to convert lowercase characters in to upper case characters:

```
#include<stdio.h>
          main()

          {
               char text[85];
               int i=0;
               printf("Enter   a   line   of   text   in
lowercase:\t");
               scanf("%[^\n]",text);
               printf("%s",text);
               printf("\n Converted to uppercase text is
:\t");
               while(text[i]!='0')
                  printf("%c", toupper(text[i]));
                   i++;
               }
                    printf("\n");
     }
```

Example 56: Reading a string with scanf.

```
#include <stdio.h>
#include <string.h>

int
main (void)
{
     char city[20], city2[20];
```

```
        printf ("What is the capital of Canada? ");
        /* the string is read with the %s placeholder */
        /* do not use & or use &city[0] */
        scanf ("%s", city);

        printf ("What is the capital of Argentina? ");
        scanf ("%s", city2);

        /* here is the report */
        printf ("\nThe capital of Canada is: %s.", city);
        printf ("\nThe capital of Argentina is: %s.", city2);

        return (0);
}
```

What is the capital of Canada? Ottawa
What is the capital of Argentina? Buenos Aires

The capital of Canada is: Ottawa.
The capital of Argentina is: Buenos.

Example 57: Reading a string with gets .

```
#include <stdio.h>
#include <string.h>

int
main (void)
{
        char city[20], city2[20];

        printf ("What is the capital of Canada? ");
        /* the string is read with gets */
        gets (city);

        printf ("What is the capital of Argentina? ");
        gets (city2);

        /* here is the report */
        printf ("\nThe capital of Canada is: %s.", city);
        printf ("\nThe capital of Argentina is: %s.", city2);

        return (0);
}
```

What is the capital of Canada? Ottawa
What is the capital of Argentina? Buenos Aires

The capital of Canada is: Ottawa.
The capital of Argentina is: Buenos Aires.

Example 58: Reading a string from a file.

```
#include <stdio.h>
#include <string.h>

int
main (void)
{
      char sentence[200];
      FILE *input;

      /* file is opened */
      input = fopen("phrase.txt", "r");

      /* the string is read from the file */
      fgets (sentence, sizeof(sentence), input);

      /* sentence is echoed on the screen */
      /* \" to display a " (double quotes) */
      printf ("The sentence is:\n\"%s\"\n\n\n", sentence);

      /* file is closed */
      fclose (input);

      return (0);
}
```


The sentence is:
"The quick brown fox."

Example 59: Comparing two strings .

```
#include <stdio.h>
#include <string.h>

int
main (void)
{

      char city1[50], city2[50];
      int comp;

      printf ("Comparison of two city names\n");
      printf ("============================\n\n");

      printf ("Enter the name of the first city (<50
letters): ");
```

```
     gets (city1);
     printf ("Enter the name of the second city (<50
letters): ");
     gets (city2);

     /* strcmp compares two strings */
     comp = strcmp (city1, city2);

     if (comp < 0)
          printf ("\n\n%s < %s.\n", city1, city2);
     else
          if (comp == 0)
               printf ("\n%s = %s.", city1, city2);
          else
               printf ("\n%s > %s.", city1, city2);

     return (0);
}
```

Comparison of two city names
==========

Enter the name of the first city (<50 letters): Vancouver
Enter the name of the second city (<50 letters): Halifax

Vancouver > Halifax.

Example 60: Manipulating strings.

```
#include <stdio.h>
#include <string.h>
#include <ctype.h>

/* This function takes a string and returns
another all in uppercase letters */
void
uppercase (char in[], char out[])
{
        int i;
        /* transforms letters in uppercase one by one */
        for (i=0; i<=strlen(in); ++i)
               out[i] = toupper(in[i]);
}


/* This function takes a string and returns
another with only the letters */
void
onlyletters (char in[], char out[])
{
        int i, j;
```

```
        /* j is the counter for the new string */
        j=0;
        for (i=0; i<=strlen(in); ++i)
        {
               /* sends char to new string only if letter */
               /* must send also the end-of-string character */
               if (isalpha(in[i]) || in[i]=='\0')
               {
                      out[j] = in[i];
                      j=j+1;
               }
        }
}


int
main (void)
{
     char before[50], after[50];

     printf ("Enter a phrase: ");
     gets (before);
     printf ("Original sentence: %s.\n", before);

     uppercase (before, after);
     printf ("In uppercase: %s.\n", after);

     onlyletters (before, after);
     printf ("Only the letters: %s.\n", after);

     return (0);
}
```


Enter a phrase: Monday, March 14, 2005
Original sentence: Monday, March 14, 2005.
In uppercase: MONDAY, MARCH 14, 2005.
Only the letters: MondayMarch.

13.4 POINTERS:

13.4.1 POINTER DATA TYPE:

When we declare a variable name m as type integer we tell the compiler that a location in memory where an integer can be stored should be found and it should be given a name m.

Thus when we write

```
int m;
```

Will pick a memory box and give it a name m. The variable name is a symbolic name for the address of the memory box. We have already used the operator & which was used in scanf function. This operator is called the address operator.

If we write &m the operator & tells the compiler to find the numeric value of the address of a memory box whose symbolic name is m.

If we write:

```
n=&m;
```

Then the address of variable m is stored in n. When a variable stores an address we declare that variable as a pointer data type.

Thus n is declared as:

```
int *n;
```

This declaration says that n will store the address of an integer variable name.

n=&m;

variable name	address	contents
m	8468	35

13.4.2 DECLARING AND INITIALIZING VARIABLES:

Since pointer variables contain addresses that belong to a separate data type, they must be declared as pointers before we use them. The declaration of a pointer variable has the following form:

```
Data type *pt_name;
```

This tells the compiler three things about the variable pt_name.

1. The asterisk(*) tells that the variable pt_name is a pointer variable.
2. pt_name needs a memory location.
3. pt_name points to variable of type data type.

For example:

```
int *q;
```

Declares the variable q as a pointer variable that points to an integer data type.

Similarly, the statement

```
float *y;
```

Declares y as a pointer to a floating point variable.

Once a pointer variable has been declared, it can be made to point to a variable using an assignment statement such as

```
p=&quantity;
```

This causes p to point to quantity. That is, p now contains the address of quantity. This is known as pointer initialization.

We must ensure that the pointer variables always point to the corresponding type of data.

Example:

```
Float a,b;
Int x, *p;
p=&a;
b=*p;
```

In the above example the result will give an error because we are trying to assign the address of a float variable to an integer pointer. Care should be taken to avoid wrong pointer assignments.

A pointer variable can be initialized in its declaration .

Example: `int x;`
`*p=&x;`

13.4.3 ACCESSING A VARIABLE THROUGH ITS POINTER:

Once a pointer has been assigned the address of a variable, the question remains as to how to access the value of the variable using the pointer. This is done by using another unary operator *(asterisk), usually known as the indirection operator. Consider the following statements:

```
int qty, *q,m;
qty=165;
q=&qty;
m=*p;
```


The first line declares qty and m as integer variables and q as a pointer variable pointing an integer. The second line assigns the value 165 to qty and the third line assigns the address of qty to the pointer variable q. The fourth line contains the indirection operator * . When the operator * is placed before a pointer variable in an expression , the pointer will return the value of the variable. The * can be called as 'value at address' . Thus the value of q would be 165. The two statements

```
q=&qty;
m=*p;
```

are equivalent to

```
m=qty.
```

Example 61: Program for accessing variables using pointers

```
main()

{
        int m,n;
        int *ptr;

        m=15;
        ptr=&m;
        y=*ptr;

        printf("Value of m is %d\n\n", m);
```

```
            printf("%d is stored at address %u \n", m,&m);
            printf("%d   is  stored  at  address   %u  \n",  &m,
&m);
            printf("%d  is  stored  at  address   %u  \n",  ptr,
&ptr);
            printf("%d is stored at address  %u \n", y, &y);
              *ptr=30;
            printf("\n Now m=%d\n",x);
}
```

Example 62: This program just demonstrates how to assign values to pointer variables. It serves no other purpose.

```
#include <stdio.h>

int
main (void)
{
     /* c and d are pointers to integers */
     int a, b, *c, *d, e;

     a = 10;
     b = a * 3;
     c = &a; /* address of a goes into c */
     d = &b; /* address of b goes into d */
     e = *c + *d; /* *c is a and *d is b */
     *d = a;
     d = &a;
     *c = *d - a % b + *c;

     printf ("Do you understand why\n");
     printf ("a= %d, b= %d, e= %d ?\n", a, b, e);

     return (0);
}
```


Do you understand why
a= 20, b= 10, e= 40 ?

Example 63: This is just a silly program playing with pointers .

```
#include <stdio.h>

int
main (void)
{
   /* a and e are integers */
   int a, e;

   /* b is a pointer to an integer */
   int* b;
```

```
    /* c is a pointer to a pointer to an integer */
    int** c;

    /* d is a pointer to a pointer to a pointer to an integer */
    int*** d;

    a = 25;    /* a contains the integer 25 */
    b = &a;    /* b contains the address of a */
    c = &b;    /* c contains the address of b */
    d = &c;    /* d contains the address of c */

    /* Do you understand that ***d is actually a? */
    e = ***d * 2;

    printf ("%d", e);

    return (0);
}
```

13.4.4 POINTERS AND ONE DIMENSIONAL ARRAYS:

When an array is declared , the compiler allocates a base address and sufficient amount of storage to contain all the elements of the array in memory locations. The base address is the location of the first element(index 0) of the array.


```
static int y[4]= {1,2,3,4,5};
```

Suppose the base address of y is defined as a constant pointer pointing to the first element , y[0] and therefore the value of y is 1000.

That is,

```
y=&y[0]=1000
```

If we declare p as an integer pointer , then we can make the pointer p to point to the array y by the following assignment:

```
p=y;
```

This is equivalent to

```
p=&y[0];
```

The relationship between p and y is shown below.

P =&y[0] (=1000)
P+1 =&y[1](=1002)
P+2 =&y[2](=1004)
P+3 =&y[3](=1006)
P+4 =&y[4](=1008)

Example 64: Program to show pointers in one-dimensional arrays:

```
main()
{
      int *p,sum,j;
      static int y[5]={4,5,7,8,0};
      j=0;
      p=y;
      sum=0;
      printf("Element value address\n\n");
      While(j<5)
      {
          printf(" y [%d]      %d     %u   \n", j, *p, p);
           sum=sum+p;
           i++;
           p++;
      }
       printf("\n Sum= %d \n", sum);
       printf("\n &x[0]=%u \n", &x[0]);
       printf(" \n p = %u \n ", p);
}
```


EXERCISES

1. What is an array? Discuss briefly the initialization of one and two dimensional arrays in C with proper examples. **[NEHU 2008]**

2. State (with justification) whether the following code segment is valid or invalid : **[NEHU 2008]**

```
int a[3]={1,2,3};
int b[3];
b=a;
```

3. What would be the output of the following code segment, if the array begins at address 1259 : . **[NEHU 2008]**

```
int i[ ]={1,2,3,4};
printf("%d %d", i, &i[0]);
```

4. Discuss the difference between call-by-value and call-by-reference with the help of suitable example. Write a program in C to swap two integers using call-by-reference technique. **[NEHU 2008]**

5. What would be the output of the following code segment? **[NEHU 2008]**

```
(i)  int x=5;                    (ii) int x=6;
```

```
     int *p=&x;                          int  *p=&x;
     printf("%d%d", ++x, *p);            printf("%d %d",++*p, p);
```

```
(iii)int x=6;
     int *p=&x;
     printf(%d %d", *&x, &*p);
```

(Note:You can assume any arbitrary memory address of x).

6. Write a program in C to compute sum of all prime numbers within the range 1 to n using function. **[NEHU 2008] [GIMT(GU) 2009]**

7. What would be the output of the following code segment? **[NEHU 2008]**

```
(i)  int x=5;                    (ii) int x=6;
     int *p=&x;                         int  *p=&x;
     printf("%d%d", ++x, *p);           printf("%d %d",++*p, p);
```

```
(iii)int x=6;
     int *p=&x;
     printf(%d %d", *&x, &*p);
```

(Note:You can assume any arbitrary memory address of x)

8. Write a C program to find the power of a given number (eg. K^n) without using pow function. **[NEHU 2009]**

9. Write short notes on: **[NEHU 2009]**
   (i) Actual and formal arguments,

   (ii)Global and 'extern' variables.

10. What is the output of the following code? Justify your answer. **[NEHU 2009]**

```
#include<stdio.h>
#define mul(x,y)  x*y
main( )
{
int p,q,r;
p=5;
q=7;
r=mul(p,q);
printf("%d",r);
r=mul(p+1,q+1);
printf("%d",r);

}
```

11. Explain general form of defining a function. **[RGU 2006]**
12. What do you mean by function call? **[RGU 2006]**
13. How are array usually processed in C? **[RGU 2006]**
14. Write a program to print multiplication table from 1 to 5**[RGU 2006]**
15. Differentiate between built in function and user defined function. Give examples. **[RGU 2006]**
16. Explain the meaning of the following declaration? **[RGU 2006]**
    (a) int *PX
    (b) char *a[12];
17. What are the difference between actual argument & formal argument? **[RGU 2006]**
18. What are pointers in C? How a pointer initialized? Explain with example? **[RGU 2006]**

CHAPTER 14

STRUCTURES, UNIONS AND FIELDS

14.1 ENUMERATED TYPES

```
enum day { sun, mon, tues, weds, thur, fri, sat } d1, d2;
enum suit { spades, hearts, clubs, diamonds } s1;
enum suit s 2, s3;
```

The identifiers in the enumerated type list can be used in assignments or tests, for example:

```
d1 = thur;
s1 = hearts;
if (d1 == sat) ...
switch (s1) {
case spades :
...
```

Each value of the enumerated type list is given an int value. If no extra information is provided by the programmer, the values start at zero and increase by one from left to right. The value of any constant in the enumeration list can be set by the programmer; subsequent enumeration constants will be given values starting from this value. There is no need for the values given to the enumeration constants to be unique.

The following (non-sensical) code fragment illustrates these three points:

```
enum day { sun=1, mon, tues, weds, thur, fri=1, sat } d1;
```

the values of the enumeration constants will be:

```
sun 1, mon 2, tues 3, weds 4, thurs 5, fri 1, sat 2
```

Enumeration constants *must* be unique across all enumerated types currently in scope; the following would be illegal:

```
enum day { sun, mon, tues, weds, thur, fri, sat } d1;
enum weekend { sat, sun } d2;
```

The base type of an enumerated type is int, and values of type int can be assigned to variables of an enumerated type, although such use may be meaningless, e.g.

```
enum day { sun, mon, tues, weds, thur, fri, sat } d1 = 76;
```

Some debuggers are able to show the values of variables of enumerated type using the identifiers used in the enumeration list, this helps with debugging. As with structures and unions, declarations of enumerated types are local to the block in which the declaration occurs.

14.2 DEFINING NEW NAMES FOR TYPES WITH *TYPEDEF*

It is possible to create new names for existing types with typedef . This is frequently used to give shorter or less complicated names for types, making programming safer and hopefully easier.

For example, consider declaring a function parameter which is a pointer to a function which itself takes an array of strings as a parameter and returns a string:

```
typedef char *string; /* string is a pointer to a char */
typedef string strfn(string []);
/* strfn is a function that takes
an array of strings as a
parameter and returns a string */
typedef strfn *pstrfn; /* pstrfn is a pointer to a strfn */
void fred(pstrfn f)
{}
```

Without using typedef the declaration would be somewhat more complicated:

```
void fred(char *(*fn)(char *[]))
{}
```

typedef declarations are local to the block in which they appear.

10.3 STRUCTURES

Structures are variables that have several parts; each part of the object can havedifferent types. Each part of the structure is called a *member* of the structure.

There are two ways to declare structured variables. You can declare a type of yourown and use that type name to declare as many variables as you wish of that type, e.g.


```
struct date {
int day, month, year, yearday;
char monname[4];
};
struct date d;
struct date d1 = {4, 7, 1776, 186, "Jul"};
```

Or you can declare the variables directly:

```
struct date {
int day, month, year, yearday;
char monname[4];
} d, d1 = {4, 7, 1776, 186, "Jul"};
```

The two declarations of d1 above show that initialisation of structures takes the same form as that of arrays.

The word following the keyword struct is the *tag* name of the structure, it gives the structure definition a type name that can be used in later declarations of variables, function parameters and return values. The tag identifier can be omitted if the type name is not needed for subsequent declarations.

Individual members of the structure are accessed by use of the . (pronounced ‘dot’) operator (as in Pascal). If the structure is accessed through a pointer, the -> operator can be used.

```
struct date {
int day, month, year, yearday;
char monname[4];
```

```
};
struct date d1;
struct date *d2 = malloc(sizeof(struct date));

d1.month = 7;
(*d2).year = 1993;
d2->year = 1993;
```

The last two statements show the alternative ways of accessing the structure through a pointer and they are exactly equivalent. The brackets are required to dereference the pointer d2 before accessing the structure element.

K&R compilers will not permit structures to be passed by value to a function or to be returned from a function (pointers must be used instead in both circumstances), nor will they allow automatic structures to be initialised. No such restrictions exist in ANSI C.

Declarations of structures and unions obey the usual scoping rules, thus it is possible to localise a declaration of a structure to a block.

Whole structures cannot be compared directly, instead a member by member comparison is needed.

10.4 UNIONS

A variable of union type may hold (at different times) objects of different types and sizes, the objects all occupying the same area of storage.

```
union tag {
members;
} variables;
For example:
union value {
int intval;
float fval;
char *pval;
} uval;
```

The variable uval can hold three different types of object, an int, a float or a string. It is the responsibility of the programmer to ensure that they access the variable in the appropriate manner.

Access to the union members is via the . operator as with structures, e.g. the data in the union above may be accessed as

```
uval.intval
uval.fval
uval.pval
```

Also, as with structures, the tag identifier can be omitted if the type is not needed for further declarations.

When initialising a union, the initialiser must be a valid initialiser for the *first* memberof the union enclosed within braces. It is only possible to initialise the int member of the example union above, e.g.

```
union value u = { 6 };
```

10.5 FIELDS

A field is a member of a structure whose bit length is specified. This can be useful for economic storage (not nearly as important as it used to be); but be warned that the code required to access bit fields becomes more complicated and so the program may have both a larger code size and also run more slowly.

```
struct {
unsigned is_keyword : 1;
unsigned is_extern : 1;
unsigned is_static : 1;
} flags;
```

Fields are also used when access to individual bits of some part of memory is required.An example might be access to the status bits of an I/O port.

Example 1: An example ofstructures.

```
#include <stdio.h>

/* the planets structure */
typedef struct
{
      char name [10];
      double diameter;
      int moons;
      double orbit, rotation;
} planets_t;

/* the solar systems structure contains a planets type element */
typedef struct
{
      double diameter;
      planets_t the_planets[9];
      char galaxy [10];
} solar_systems_t;

int
main(void)
{
planets_t planet = {"Earth", 1000, 1, 1.0, 24.0};
solar_systems_t solarsystem;

printf ("The planet %s has %d moon(s).\n", planet.name,
planet.moons);

solarsystem.the_planets[2] = planet;

strcpy (planet.name, "Jupiter");
```

```
planet.diameter = 142980;
planet.moons = 16;
planet.orbit = 11.9;
planet.rotation = 9.925;

printf ("Planet %s has %d moon(s).\n", planet.name,
planet.moons);
printf ("Planet %s has %d moon(s).\n",
solarsystem.the_planets[2].name,
                        solarsystem.the_planets[2].moons);

return(0);

}
```

The planet Earth has 1 moon(s).
The planet Jupiter has 16 moon(s).
The planet Earth has 1 moon(s).

Example 2: Using functions with structures.


```
#include <stdio.h>
#include <string.h>

typedef struct
{
        char name [20];
        double diameter;
        int moons;
        double orbit;
        double spin;
} planets_t;


/* structure sent to function */
void
print_planet (planets_t p)
{
        printf ("-----------------------------------------------
------\n");
        printf ("%s\n", p.name);
        printf ("Diameter: %.1f km\n", p.diameter);
        printf ("Number of moons: %d\n", p.moons);
        printf ("Time to complete one orbit around the sun: %.1f
years\n", p.orbit);
        printf ("Time to complete one rotation on the axis: %.1f
hours\n", p.spin);
        printf ("-----------------------------------------------
------\n\n");
}


/* structure returned by value */
```

```
planets_t
get_planet (void)
{

        planets_t pl;

        printf ("Enter the planet's name: ");
        scanf ("%s", pl.name);
        printf ("Enter the planet's diameter in km: ");
        scanf ("%lf", &pl.diameter);
        printf ("How many moons orbit this planet? ");
        scanf ("%d", &pl.moons);
        printf ("How many years does it take for this planet to
orbit the sun? ");
        scanf ("%lf", &pl.orbit);
        printf ("How many hours for one rotation around the axis?
");
        scanf ("%lf", &pl.spin);

        return (pl);
}

int
main (void)
{
         planets_t planet, planets[10];

         /* filling planet variable */
         planet =  get_planet ();

         /* filling cell 2 of planets array */
         planets[2] = get_planet ();

         /* displaying record of planet 2 */
         print_planet (planets[2]);

         /* displaying record of planet variable */
         print_planet (planet);

         /* copying planet variable into planet 0 */
         planets[0] = planet;

         /* displaying record of planet 0 */
         print_planet (planets[0]);

         return(0);
}
```


Enter the planet's name: Earth
Enter the planet's diameter in km: 12000
How many moons orbit this planet? 1
How many years does it take for this planet to orbit the sun? 1
How many hours for one rotation around the axis? 24
Enter the planet's name: Saturn
Enter the planet's diameter in km: 120000

How many moons orbit this planet? 23
How many years does it take for this planet to orbit the sun? 29.7
How many hours for one rotation around the axis? 10.5

Saturn
Diameter: 120000.0 km
Number of moons: 23
Time to complete one orbit around the sun: 29.7 years
Time to complete one rotation on the axis: 10.5 hours

Earth
Diameter: 12000.0 km
Number of moons: 1
Time to complete one orbit around the sun: 1.0 years
Time to complete one rotation on the axis: 24.0 hours

Earth
Diameter: 12000.0 km
Number of moons: 1
Time to complete one orbit around the sun: 1.0 years
Time to complete one rotation on the axis: 24.0 hours

EXERCISES

1. What is user defined data types? Give examples.
2. What is structure in C? Explain with an example.
3. What is union in C? Explain with an example.
4. Explain the difference between structure and union.
5. Write a program to display student records such as name, roll no., branch, address, marks etc. **[GIMT(GU) 2008]**
6. Write a program to display employee information such as name, id., department, address, salary etc. **[GIMT(GU) 2009]**

CHAPTER 15

FILES

15.1 FILES INTRODUCTION

The programs that we developed up to now were neither able to produce permanent output nor were they able to read data inputs other than from the keyboard. Using files you can save your output data permanently and retrieve them later.

A file in general is a collection of related records, such as student information, marks obtained in an exam, employee salaries, etc. Each record is a collection of related items called fields, such as "student name", "date of birth", "subjects registered", etc. The common operations associated with a file are:

Read from a file (input)
Write to a file (output)
Append to a file (write to the end of a file)
Update a file (modifying any location within the file)

In C language data is transferred to and from a file in three ways:

Record input /output (one record at a time)
String input/output (one string at a time)
Character input/output (one character at a time)

15.2 THE FILE PROTOCOL

Accessing a file is a three step process:

Opening a connection to a file
Reading/writin g data from/to the file
Closing the connection

15.2.1 OPENING A CONNECTION TO A FILE

In order to use a file on a disk you must establish a connection with it. A connection can be established using the fopen function. The function takes the general form:

```
fopen(file_name, access_mode)
```

The file_name is the name of the file to be accessed and it may also include the path. The access_mode defines whether the file is open for reading, writing or appending data. The access modes supported by fopen function are as follows.

Access mode	Description
"r"	Open an existing file for reading only.
"w"	Open a file for writing only. If the file does not exist create a new one. If the file exists it will be overwritten.

"a"	Open a file for appending only. If the file does not exist create a new one. New data will be added to the end of the file.
"r+"	Open an existing file for reading and writing
"w+"	Open a new file for reading and writing
"a+ "	Open a file for reading and appending. If the file does not exist create a new one.

The following code opens a file named "my file.txt" in the current directory for appending data:

```
FILE *fp;
fp = fopen("my file.txt", "a");
```

The function fopen returns a pointer (referred as the file pointer) to the structure FILE which is defined in the stdio.h headier file. When you open a file it would be better to make sure that theoperation is successful. If the establishment of a connection is successful the function returns a pointer to the file. If an error is encountered while establishing a connection the functions returns NULL.

15.2.2 CLOSING THE CONNECTION TO A FILE

After a connection to a file is established it can be used to read or write data. When all the file processing is over the connection should be closed. Closing the connection is important as it writes any remaining data in the buffer to the output file. The function fclose is used to close the file.

For example:

```
fclose(fp)
```

When closing the file the file pointer "fp" is used as an argument of the function. When a file is successfully closed the function fclose returns a zero and any other value indicates an error.

15.2.3 READING DATA FROM A FILE

When reading data from a ASCII file you can either read one character or one string at a time.

Reading Characters from a File

To read one character at a time you can use the getc function. It takes the form:

getc(file_pointer)

You can assign the output of the function getc to an int or char variable.

Example 1: Write a program to read the file "my file.txt" which has the message:

Hello World!
This is my first file

The following program reads the file "my file.txt" one character at a time and displays it on the screen.

```
/* Program-9.1 */
#include <stdio.h>
int main()
{
```

```
FILE *fp;
char c;

fp = fopen("my text.txt", "r"); //open read-only if(fp !=
NULL)
{

while ( c != EOF)
{
printf("%c",c); c= getc(fp);
}
fclose(fp);
}
else

//read the 1st character
//if not the end of file
//read next character //close the file

printf("\nError while opening file...");
return 0;
}
```

Hello World!
This is my first file

In Example1 a connection is first established to the file. Then the expression if(fp != NULL) evaluates whether the connection is successful. If it is not successful the program will display the message "Error while opening file..." If it is successful it reads the first character from the file.

If the character is not the end of the file (indicated by the End Of File (EOF) mark) it displays the character. Then the program continues to read the rest of the characters in the file until it finds the EOF mark. Afterwards the connection to the file is closed using the fclose function.

Reading a String from a File

In real-life applications it is more useful to read one string at a time rather than one character. With every read, the program has to check for the line feed (LF) character so it can find the end of each string. Also it must check for the EOF mark which comes at the end of the file. The fgets function can be used to read a string at a time. The function generally takes the form:

```
fgets(string, max_characters, file_pointer)
```

The "string" is a character array (also called a character buffer) and "max_characters" define the maximum number of characters to read form a line. The function fgets returns a char pointer. It returns NULL if EOF mark is encountered. One deficiency in fgets is that it can only read to a fixed character buffer, therefore you need to know in advance the maximum number of characters in a string.

Example 2: Modify Program-15.1 such that it uses the fgets function instead of fgetc function. Suppose the file does not have more than 100 characters in a line.

```
#include <stdio.h>

int main()
{
FILE *fp;
char buffer[100];   //char array with 100 elements
char *result;  // hold the result of the fgets function

fp = fopen("my text.txt", "r"); //open read-only if(fp != NULL)
{
result = fgets(buffer, 100, fp); //read the 1st string
while(result != NULL)    //if not the end of file
{
printf("%s",buffer);
result = fgets(buffer, 100, fp); //read the next string
}
fclose(fp);    //close the file
}
else
printf("\nError while opening file");
return 0;
}
```


15.2.4 WRITING DATA TO A FILE

You can also write data to file either one character at a time or a string at a time.

Writing Character to a File

To write a character to a file the putc function can be used. It has the form:

putc(c, fp)

where c is the character while fp is the file pointer. It returns an int value which indicates the success or the failure of the function. It returns the int value of the character if it is successful, if not it returns

EOF mark.

Example 3: Write a C program to store the message "Introduction C Programming" in a file named "message.txt".

Program 3 is an implementation of the above requirement. The function putc is used to write characters in the message to the file. To find the number of characters in the message the strlen function which returns the number of characters in a string is used. A pointer is used to point to the string and the pointer is incremented by one memory location at a time.

```
/* Program 3  */
#include <stdio.h>
#include <string.h>
int main()
{
FILE *fp;
```

```
int i;    //loop counter
char *message;
message = "Introduction C Programming";

fp = fopen("c:\\message.txt", "w"); //open for writing
if(fp != NULL) //if success
{
for (i =0 ; i < strlen(message);i++)
putc(*(message+i),fp); //write character pointed by pointer
fclose(fp);    //close the file
}
else
printf("\nError while opening file");

return 0;
}
```

Writing a String to a File

The advantage of putc is that it allows you to control every byte that you write into the file. However sometimes you may want to write one string at a time. Two functions, namely fputs and fprintf can be used for this purpose. The fprintf function is identical to the printf function only difference being that it writes to a file rather than to the screen. The format of each function is:

```
fputs(string, file_pointer)
fprintf(file_pointer, "%s", string)
```


Exercise 1 - Modify Program-3 such that it uses the fputs rather than the fputc function to write the message to the file.

Exercise 2 - Develop a simple telephone directory which saves your friends contact information in a file named directory.txt. The program should have a menu similar to the following:

----------Menu----------
1. Add new friend.
2. Display contact info.
3. Exit

Enter menu number:
When you press "1" it should request you to enter following data:
---------New friend info--------
Name : abcd
Phone-No: 12345
e-Mail : abcd@yahoo.com

After adding new contact information it should again display the menu. When you press "2" it should display all the contact information stored in the directory.txt file as follows:

----------Contact info----------
Name Tel-No e-Mail
xyz 56789 xyz@yahoo.com
uvw 45678 uvw@gmail.com
abcd 12345 abcd@yahoo.com

Example 4: This program calculates the average of all the numbers in a file of integers.

```
#include <stdio.h>

int
main (void)
{
     int number, sum, count;
     double average;
     FILE *in;

     in = fopen ("numbers.data", "r");

     /* sums and counts must always be initialized to zero */
     sum = 0;
     count = 0;

     /* read number by number until the end of file */
     while (fscanf (in, "%d", &number) != EOF)
     {
          /* count and sum the numbers */
          sum = sum + number;
          count = count + 1;
     }
     fclose (in);

     /* final report */
     printf ("There are %d numbers in the file.\n", count);
     printf ("The sum of all the numbers is %d.\n", sum);
     average = (double)sum / count;
     printf   ("There   average   of   all   the   numbers   is
%5.2lf.\n", average);

     return (0);
}
```


numbers.data: 11 18 5 101 6 78 47 3
There are 8 numbers in the file.
The sum of all the numbers is 269.
There average of all the numbers is 33.63.

Example 5: Birdwatching program (fixed loop / file input) .

```
#include <stdio.h>

int
main (void)
{
```

```
    FILE *birdfile;
    int birds, days, total, i, j;

    birdfile = fopen ("birds.txt", "r");
    total = 0;

    /* loop goes though all 12 months */
    for (i=1; i<=12; ++i)
    {
       /* reading the number of days of sightings */
       fscanf (birdfile, "%d", &days);

       /* loop varies with number of days of sightings */
       for (j=1; j<=days; ++j)
       {
          /* reading the number of birds */
          fscanf (birdfile, "%d", &birds);
          total = total + birds;
       }
    }

    fclose (birdfile);
    printf ("Total number of birds sighted: %d\n", total);

    return(0);
}
```

Total number of birds sighted: 219

3 4 6 7
3 1 1 1
1 1
0
7 1 5 9 11 5 4 1
2 9 1
1 3
8 2 4 6 9 12 23 4 12
6 4 6 3 9 4 11
3 2 3 7
1 9
2 9 10

Example 6: Birdwatching program (EOF/file input/feof) .

```
#include <stdio.h>

int
main (void)
{
   FILE *birdfile;
```

```
   int birds, days, total, i, j;

   birdfile = fopen ("birds.txt", "r");
   total = 0;

   fscanf (birdfile, "%d", &days); /* reads first number in
the file */

   /* loop goes while there is data to read */
   while (!(feof (birdfile)))
   {

      /* loop varies with number of days of sightings */
      for (j=1; j<=days; ++j)
        {
           fscanf (birdfile, "%d", &birds);
           total = total + birds;
        }

      /* update - reading again */
      fscanf (birdfile, "%d", &days);
   }

   fclose (birdfile);
   printf ("Total number of birds sighted: %d\n", total);

   return(0);
}
```


Total number of birds sighted: 219

3 4 6 7
3 1 1 1
1 1
0
7 1 5 9 11 5 4 1
2 9 1
1 3
8 2 4 6 9 12 23 4 12
6 4 6 3 9 4 11
3 2 3 7
1 9
2 9 10

Example 7: Birdwatching program (EOF/file input/status var).

```
#include <stdio.h>

int
main (void)
{
   FILE *birdfile;
   int birds, days, total, i, j, status;

   birdfile = fopen ("birds.txt", "r");
   total = 0;

   /* initialization - reading 1st value */
   status = fscanf (birdfile, "%d", &days);

   while (status != EOF) /* loop goes while there is data */
   {

     /* loop varies with no of days of sightings */
     for (j=1; j<=days; ++j)
     {
        fscanf (birdfile, "%d", &birds);
        total = total + birds;
     }

      /* update - reading again */
      status = fscanf (birdfile, "%d", &days);
   }

   fclose (birdfile);
   printf ("Total number of birds sighted: %d\n", total);

   return(0);
}
```


Total number of birds sighted: 219

3 4 6 7
3 1 1 1
1 1
0
7 1 5 9 11 5 4 1
2 9 1
1 3
8 2 4 6 9 12 23 4 12
6 4 6 3 9 4 11
3 2 3 7
1 9
2 9 10

Example 8: Birdwatching program (EOF loop, no status var).

```
#include <stdio.h>

int
main (void)
{
   FILE *birdfile;
   int birds, days, total, i, j;

   birdfile = fopen ("birds.txt", "r");
   total = 0;

   /* loop goes while there is data */
   while (fscanf (birdfile, "%d", &days) != EOF)
   {

     /* loop varies with no of days of sightings */
     for (j=1; j<=days; ++j)
     {
        fscanf (birdfile, "%d", &birds);
        total = total + birds;
     }
   }

   fclose (birdfile);
   printf ("Total number of birds sighted: %d\n", total);

   return(0);
}
```


Total number of birds sighted: 219

3 4 6 7
3 1 1 1
1 1
0
7 1 5 9 11 5 4 1
2 9 1
1 3
8 2 4 6 9 12 23 4 12
6 4 6 3 9 4 11
3 2 3 7
1 9
2 9 10

Example 9: Working with multiple files (This program contains a few syntax errors. Try to correct them).

```
#include <stdio.h>
#define PI 3.1416

int
main (void)
{
      int a, b, c, d, e, total;
      FILE *f1, *f2, *f3;

      /* opening input files */
      f1 = fopen ("file1.dat", "r");
      f2 = fopen ("file2.dat", "r");

      /* reading data */
      fscanf (f1, "%d%d%d", &a, &b, &c);
      fscanf (f2, "%d%d%, &d, &e);

      /* adding the numbers */
      total = a + b + c + d + e;

      /* closing input files */
      fclose (f1);
      fclose (f2);

      /* opening output file */
      f3 = fopen ("total.dat", "w");

      /* output report on both screen and file */
      printf ("Read from first file: %d %d %d\n", a, b, c);
      printf ("Read from second file: %d %d\n", d, e);
      printf ("The sum is: %d\n\n", total);
      fprintf ("f3, "%d", total);
      printf ("\nFILE total.dat CREATED.\n");
      /* check your directory for the new file! */

      /* closing output file */
      fclose (f3);

      return (0);
}
```


Read from first file: 34 78 122
Read from second file: 45 90
The sum is : 369

FILE total.dat CREATED.

EXERCISES

1. What is file? How it is created in C?
2. Describe briefly different file accessing modes.
3. What is the significance of EOF?
4. Write a program to store student records such as name, roll no., branch, address, marks etc. in a file and display it.
5. Write a program to store employee information such as name, id., department, address, salary etc. in a file and display it.

CHAPTER 16

INTRODUCTION TO C++ AND OBJECT ORIENTED PROGRAMMING

16.1 INTRODUCTION

C++ is a superset of C. It adds to the C language the capability to implement Object Oriented Programming (OOP). Object oriented programming is a way of organizing programs. The emphasis is on the way programs are designed. OOP programs are organized around objects which contains both data and functions that act on that data.

A major building block of C++ programs is the functions. As like C, in C++, the function main() is always the first one executed when the program is executed. Each statement in C++, like in C, ends with a semicolon. A statement may contain one or more expressions, which are sequences of variables and operators that usually evaluate a specific value.

16.2 THE ORIGINS OF C++

C++ was developed by Bjarne Stroustrup of AT&T Bell Laboratories in the early 1980's, and is based on the C language. The name is a pun - "++" is a syntactic construct used in C (to increment a variable), and C++ is intended as an incremental improvement of C. Most of C is a subset of C++, so that most C programs can be compiled (i.e. converted into a series of low-level instructions that the computer can execute directly) using a C++ compiler.

C is in many ways hard to categorize. Compared to assembly language it is high-level, but it nevertheless includes many low-level facilities to directly manipulate the computer's memory. It is therefore an excellent language for writing efficient "systems" programs. But for other types of programs, C code can be hard to understand, and C programs can therefore be particularly prone to certain types of error. The extra object-oriented facilities in C++ are partly included to overcome these shortcomings.

16.3 AN EXAMPLE C++ PROGRAM

Here is an example of a complete C++ program:

```
     /* This program prompts the user for the current year,
the user's
     current age, and another year. It then calculates the
age
     that the user was or will be in the second year
entered. */

     #include <iostream>

     using namespace std;

     int main()
     {
          int year_now, age_now, another_year, another_age;

          cout << "Enter the current year then press
RETURN.\n";
```

```
          cin >> year_now;

          cout << "Enter your current age in years.\n";
          cin >> age_now;

          cout << "Enter the year for which you wish to
know your age.\n";
          cin >> another_year;

          another_age = another_year - (year_now -
age_now);

          if (another_age >= 0) {
               cout << "Your age in " << another_year << ":
";
               cout << another_age << "\n";
          } else {
               cout << "You weren't even born in ";
               cout << another_year << "!\n";
          }

          return 0;
     }
```


This program illustrates several general features of all C++ programs. It begins (after the comment lines) with the statement

```
#include <iostream>
```

This statement is called an include directive. It tells the compiler and the linker that the program will need to be linked to a library of routines that handle input from the keyboard and output to the screen (specifically the cin and cout statements that appear later). The header file "iostream" contains basic information about this library. You will learn much more about libraries of code later in this course.

After the include directive is the line:

```
using namespace std;
```

This statement is called a *using* directive. The latest versions of the C++ standard divide names (e.g. cin and cout) into subcollections of names called *namespaces*. This particular *using* directive says the program will be using names that have a meaning defined for them in the std namespace (in this case the iostream header defines meanings for cout and cin in the std namespace).

Some C++ compilers do not yet support namespaces. In this case you can use the older form of the include directive (that does not require a *using* directive, and places all names in a single global namespace):

```
#include <iostream.h>
```

Much of the code you encounter in industry will probably be written using this older style for headers.

Because the program is short, it is easily packaged up into a single list of program statements and commands. After the include and using directives, the basic structure of the program is:

```
int main()
{
     First statement;
     ...
     ...
     Last statement;

     return 0;
}
```

All C++ programs have this basic "top-level" structure. Notice that each statement in the body of the program ends with a semicolon. In a well-designed large program, many of these statements will include references or calls to sub-programs, listed after the main program or in a separate file. These sub-programs have roughly the same outline structure as the program here, but there is always exactly one such structure called main. Again, you will learn more about sub-programs later in the course.

When at the end of the main program, the line

```
return 0;
```

means "return the value 0 to the computer's operating system to signal that the program has completed successfully". More generally, *return statements*signal that the particular sub-program has finished, and return a value, along with the flow of control, to the program level above. More about this later.

Our example program uses four *variables*:

```
year_now, age_now, another_year and another_age
```

Program variables are not like variables in mathematics. They are more like symbolic names for "pockets of computer memory" which can be used to store different values at different times during the program execution. These variables are first introduced in our program in the variable declaration

```
int year_now, age_now, another_year, another_age;
```

which signals to the compiler that it should set aside enough memory to store four variables of type "int" (integer) during the rest of the program execution. Hence variables should always be declared before being used in a program. Indeed, it is considered good style and practice to declare all the variables to be used in a program or sub-program at the beginning. Variables can be one of several different types in C++, and we will discuss variables and types at some length later.

16.4 OBJECT ORIENTED PROGRAMMING FEATURES OF C++

All the traditional programming constructs of C language discussed in previous chapters related to C programming are also supported by C++. In addition C++ as an extension of C supports the object oriented programming features. In the following sections we discuss briefly some of the major OOP features of C++ like

-Data abstraction and Encapsulation
-Operator Overloading
-Inheritance
-Polymorphism etc.

16.4.1 Data abstraction and Encapsulation

Data abstraction means hiding internal complexities related to data representation and implementation etc. and to provide the user with a friendly interface to use the data without knowing the internal complexities. Encapsulation implements data abstraction. Encapsulation is wrapping data functions that act on those data in a single bundle.

In C++ data abstraction and encapsulation is implemented by *classes* and *objects*. A *class* can be said as general entity that includes the data and function definitions that act on those data. An object is a special instance of the class. Let us see the following example.

Example 1: Use of class and objects.

```
#include<iostream.h>
class test
{
   private:
     int data1;
     int data2;
   public:
     void input_function()
     {
       cout<<"Enter first data;
      cin>>data1;
      cout<<"Enter second data;
      cin>>data2;
     }

     public output_function()
     {
       cout<<"The data are:"<<data1<<data2;
             }
};

int main()
{
  test object1,object2;
  object1. input_function();
  object1. output_function();
  object2. input_function();
  object2. output_function();
}
```

Here the class name is test. It includes two data member data1 and data2 written under private and two member functions input_function() and output_function() that act on the data members data1 and data2 written under public. The keywords private, public etc are called access specifiers will be discussed next. As it can be seen all complexities are included inside the class. In main() only the objects object1 and object2 are crated and the member functions are invoked on these objects to get the job done.

Access Specifiers private, protected and public:

To implement data hiding the data are concealed within a class so that it can not be accessed by functions mistakenly outside the class. private, protected and public are the different types of protections available within a class called access specifiers .

Members marked *private* can only be accessed by functions defined as a part of the class. Data are most often defined as private.

Public members can be accessed from anywhere in the program. Member functions are usually public. In general data are not declared as public.

Another type of protection available within a class is *protected.* Members declared as *protected* are private within a class and are available for private access in derived classes. Derived classes are related to inheritance and will be discussed later.

16.4.2 Operator Overloading

Operator overloading is the OOP feature that enables to redefine some existing operators to perform newly defined operation by user. For example + operator can be overloaded to add two objects. The following example adds two currency objects.

Example 2: Illustrating Operator Overloading.

```
#include<iostream.h>
class currency
{
private:
     int rupees;
     int paise;
public:
     void getdata()
     {
     cout<<"Enter Rupees";
     cin>>rupees;
     cout<<"Enter paise";
     cin>>paise;

     void displaydata()
     {
          cout<<rupees<<"."<<paise;
     }

          currency operator +(currency c)
          {
               int r=rupees+c.rupees;
               int p=paise+c.paise;
while(paise>100)
```

```
            {
paise=paise-100;
rupees++;
            }
      return currency(r,s);
}
      main()
      {
      currency c1,c2,c3;
      c1.getdata();
      c2.getdata();
      c3=c1+c2;
      c3.displaydata();
      }
```

Here + operator is redefined to add two currency.

16.4.3 Inheritance

Inheritance is the process of creating new classes from existing classes. The new class is called derived class and the existing class is called base class. The derived class inherits all the capabilities of the base class but can add properties of its own. The base class is unchanged by this process.

Inheritance can be single, multiple, multilevel, hybrid etc. If the class is derived from single base class then it is single inheritance, if from multiple base classes than multiple inheritance and if a class is derived from another derived class then it is multilevel inheritance. Hybrid inheritance is a combination of all these.

The following example illustrates the concept of inheritance.

Example 3: Illustrates concept of Inheritance.

```
#include< iostream.h>
#include< conio.h>

class student
{
private :
int rn;
char na[20];
public:
void getdata()
{
cout< < "Enter Name And Roll No : ";
cin>>na>>rn;
}
void putdata()
{
cout< < endl< < na< < "\t"< < rn< < "\t";
}
};

class test : public student
{
protected:
float m1,m2;
```

```
public:
void gettest()
{
cout< < endl< < "Enter your marks In CP 1 And Cp 2 :";
cin>>m1>>m2;
}
void puttest()
{
cout< < m1< < "\t"< < m2< < "\t";
}
};

class sports
{
protected:
float score;
public:
void getscore()
{
cout< < endl< < "Enter your score :";
cin>>score;
}
void putscore()
{
cout< < score< < "\t";
}
};



class results : public test , public sports
{
private :
float total;
public :
void putresult()
{
total = m1+m2+score;
cout< < total;
}
};

void main()
{
results s[5];
clrscr();
for(int i=0;i< 5;i++)
{
s[i].getdata();
s[i].gettest();
s[i].getscore();
}
cout< < "_____"< <
endl;
```

```
cout< < endl< < "Name\tRollno\tCP 1\tCP 2\tScore\tTotal"< <
endl;
cout< < "-----------------------------------------"< <
endl;
for(i=0;i< 5;i++)
{
s[i].putdata();
s[i].puttest();
s[i].putscore();
s[i].putresult();
}
cout< < endl< < "----------------------------------------
----";
getch();
}
```

16.4.4 Polymorphism

Polymorphism means many forms. In C++ polymorphism means the ability to access different implementations of a function using the same name. Polymorphism can be compile time or runtime. Example of a compile time polymorphism is operator overloading.

Run time polymorphism is based on virtual functions. Virtual functions are the functions which are declared with the keyword virtual in the base class. Such function may or may not be implemented in derived classes. If implemented, the declaration must be identical except the word virtual. The following program illustrates run time polymorphism using virtual functions.

Example 4: Program showing runtime Polymorphism.

```
#include <iostream>
using namespace std;

class CPolygon {
     protected:
    int width, height;
  public:
    void set_values (int a, int b)
      { width=a; height=b; }
    virtual int area ()
      { return (0); }
  };

class CRectangle: public CPolygon {
  public:
    int area ()
      { return (width * height); }
  };

class CTriangle: public CPolygon {
  public:
    int area ()
      { return (width * height / 2); }
  };
```

```
int main () {
  CRectangle rect;
  CTriangle trgl;
  CPolygon poly;
  CPolygon * ppoly1 = &rect;
  CPolygon * ppoly2 = &trgl;
  CPolygon * ppoly3 = &poly;
  ppoly1->set_values (4,5);
  ppoly2->set_values (4,5);
  ppoly3->set_values (4,5);
  cout << ppoly1->area() << endl;
  cout << ppoly2->area() << endl;
  cout << ppoly3->area() << endl;
  return 0;
}
```

EXERCISES

1. Compare C and C++ with respect to various features.
2. What is OOP? What are the characteristics of OOP?
3. C++ is an OOP language. Justify.
4. Discuss the following taking examples in C++.

   (a) Operator Overloading

   (b) Inheritance

   (c) Polymorphism

Table of Contents

Emotional Intelligence of Mid-Level Service Manager on Career Success: An Exploratory Study

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Abstract:
Career success has been visualized as an outcome of multifaceted variables that operate both intrinsic and extrinsic domain of organizational ecosystem. Emotional intelligence is the state of mind how a person behaves rationally and logically in variety of emotional setup. The impact of emotional intelligence varies with profile and level of jobs. The study shows that the higher EI is highly related to greater accomplishment of jobs as we proceed to superior job responsibility. In the organizational hierarchy, the mid-level professionals are in between and focal layer of both the top-down and bottom-up approach. The rapid changes of roles as a mediating agent between top management, lower management and at the same time to play the role of transforming agent of the instructions from higher-ups to the lower ends are the testimony of high emotional intelligence behavioural components.
The paper has attempted to unearth how the emotional intelligence are related to the career success particularly for the mid-level executives in the north-eastern region. This paper is empirical in nature based on primary as well as secondary information. The study result reflects that emotional intelligence has significant impact on achieving subjective career success among the respondents in the study region. However, the intensity of the impact (R^2 value) may vary with the changing prospective of organizational climate and other temporal factors.

Keywords: *Career success, Emotional Intelligence, Mid-level service manager, north-eastern region.*

1. Introduction

Career is a complex term, and different authors define it in different ways. In the past, people did not consider complex and important as now, and it was considered that when a person had a job, it was for a life long term (Bosionoles, 2004).

Career success has been defined as "the positive psychological or work-related outcomes or achievements one accumulates as a result of work experiences" (Seibert, Crant and Kraimer, 1999: 417). Mirvis and Hall (1994, p. 366) define career success as "the experience of achieving goals that are personally meaningful to the individual, rather than those set by parents, peers, an organization, or society". Dany (2003) provides an alternative theory, that people's definitions of career success are fashioned on an on-going basis throughout their lives, and subsequently change whenever changes in their personal lives have an impact on their priorities.

Career success is a result of a person's career experiences and involves the individual's evaluation of desirable work-related outcomes at any point during these experiences (Arthur et al., 2005; Gattiker and Larwood, 1990; Hennequin, 2007; Judge and Bretz, 1994;Poon, 2004).

Career success is of importance to individuals because of the positive outcomes (e.g., promotion, salary level, job satisfaction, and career satisfaction) associated with it (Judge, Higgins, Thorensen, & Barrick, 1999). It is also important to organizations because successful employees have the capacity to add value that influences organizational performance (Delaney &Huselid, 1996). For this reason, its prediction has attracted considerable research interest.

Mirvis and Hall (1994) define career success as "the experience of achieving goals that are personally meaningful to the individual, rather than those set by parents, peers, an organization, or society". Bozionelos (2008) defined career success expectation as the expected future achievements of employees in their work lives.

Boudreau, Boswell, and Judge (2001) define career success as 'the accomplishment of desirable work-related outcomes at any point in a person's work experiences over time.' Empirical studies on the assessment of careers based on the concept of career success all agree that it is difficult to define and measure career success. The reason is that career success cannot be objectively determined and cannot be measured solely using external criteria such as hierarchical position and salary level because several subjective factors also intervene. As a result, there is no consensus on what constitutes career success. Arthur, Khapova, and Wilderom (2005), in a comparative study of 80 papers, divide the existing literature into three groups: in the first group it is argued that objective career success affects subjective career success; the second attributes a predominant role to subjective career success over objective career success; and a third group of papers holds that the subjective and objective aspects of career success are interdependent. More recently, Dries (2011) provides a detailed review of the concepts of career success, which appear in the most relevant research studies on this subject, revealing a wide variety of definitions, measurement methods and determining variables.

1.1. Objectives of the Study

i. To identify the set of variables that can influence career success of professionals belonging to that segment using existing literatures.

ii. To study the effect of emotional intelligence on career success among the middle level managers in the study region.

2. Literature Review

Emotional intelligence can actually be more influential upon an individual's success in life (personally and professionally) than cognitive intelligence (Stewart, 2008). People with high levels of emotional intelligence abilities are more likely than who have less emotional intelligence to achieve high levels of success in their workplace. Specially, scholars have stated that social skills are necessary for executive level leaders; as individuals ascend the organizational hierarchy; social intelligence becomes a relevant determinant increasingly of who will and will not be successful (Carmeli, 2003). Emotional intelligence is also an important of personal relationships success, family functioning, and success in the workplace (Salovey, Mayer & Causo, 2002). It's found that the emotionally intelligence people have enjoyed more career success, feel less job insecurity, lead more effectively, are more adaptable to stressful events, possess better coping strategies and indicate greater sales success than those who have low emotional intelligence (Yousuf & Ahmad, 2007). Goleman focuses on the importance of emotional intelligence in general work success of people and achievement in their life. Other researchers since Goleman have claimed that emotional intelligence can predict important occupational and educational variables (Fisher & Ashkanasy, 2000). The importance of emotional intelligence to individual and career success can be explained by how important relationships have become in evaluating personal and organizational success (Robbins, 2005). Emotionally intelligence people are able to be effective in pursing the right career that is a career that matches the values, goals, and vision of the individual. Furthermore, it is believed that individuals who have high levels of emotional intelligence will have higher levels of job

satisfaction and organizational commitment, that will make both the individuals and organizations more successful (Stewart, 2008).

3. Research Methodology

The study was undertaken to understand the effect of emotional intelligence on career success among the mid-level managers from the service sector working in Arunachal Pradesh. The study was exploratory in nature with empirical arguments. The study was carried out using both primary as well as secondary information. For primary information a structured questionnaires were used to collect the data from the sample population. For secondary information appropriate domain literatures, various reports were used. Total sample size was 100 mid-level service managers, which have been collected from various sectors of service industries as per the convenience of the researcher.

The collected data were tabulated in the SPSS version 21 for the processing and analyzing of data. Descriptive statistics, parametric and non-parametric test were done to achieve the objectives of the study.

4. Analysis and Interpretation

4.1. Analysis-1

Table 1- Other set of variables influencing career success

`Sl. No.	Variables	Key Findings	Citations
1	Personality (5-factor personality trait)	Positive relationship between conscientiousness and career success.	*Judge et al., (1999);*
		Extroversion and its facets appear to be positively related to extrinsic career success.	*Rawls and Rawls (1968)*
2	Political Skill	The study was to investigate the relations between political skill (the overall construct and the four dimensions) and five career-related outcomes. It was found that the overall political skill variable was a powerful predictor, but that the predictive power of this variable was primarily driven by the networking ability dimension.	*Todd, S. Y. et. al. (2001);*
		Study outcome shows that stronger works councillors' political skill, the more successful they were in their career.	*Blickle et al., (2010).*
3	Gender	Gender has influenced on career success. Gender moderated the predictive influence of international experience on compensation, ascendancy, and perceived success. The findings also illustrate that career development models should be situated by (private versus public) sector and specify systemic gender differences in career success outcomes.	*Orser & Leck, J. (2010).*
4	Self-	Our results, based	*Kammeyer - Muell*

	esteem	on a cross-lagged regression design, suggest that self-esteem increases occupational prestige and income.	*er, J. D. et. al (2008)*
5	Mentoring	Mentoring includes coaching, support, and sponsorship, which provide the protégés the technical and interpersonal skills, and visibility opportunities that enable them to succeed in their careers.	*Whitely, Dougherty & Dreher, 1991*
6	Human capital	It is suggested that person- environment fit and organizational support are important antecedents of career success. Knowledge of career changes and these antecedents help individuals and organizations manage career success.	*Ballout, H. I. (2007)*
7	Networking	Networking is related to concurrent salary and that it is related to the growth rate of salary over time. Networking is also related to concurrent career satisfaction. As satisfaction remained stable over time, no effects of networking on the growth of career satisfaction were found.	*Wolff & Moser (2009)*

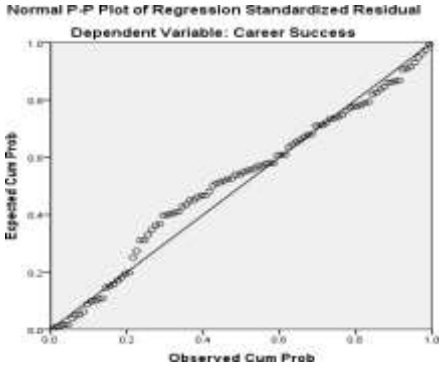
Analysis – 2

Table 2 - Correlations

		Emotional Intelligence	Career Success
Emotional Intelligence	Pearson Correlation	1	.328**
	Sig. (1-tailed)		.000
	N	100	100
Career Success	Pearson Correlation	.328**	1
	Sig. (1-tailed)	.000	
	N	100	100

**. Correlation is significant at the 0.01 level (1-tailed).

Analyzing the data set it is found that, there is a positive relationship between career success with emotional intelligence. However the correlation coefficient 'r' is 0.328 which is somehow lesser than the expected in consonance with established theoretical framework. This may be interpreted that study area is in the formative stage and number of middle level managers and number of firms belongs to organized sector are quite less even among the northeastern states so impact of emotional intelligence towards career success has not been adequately translated. However if similar studies can be conducted after 3 – 4 years it is expected that the value of 'r' would be more significant.



In the P.P Plot diagram, it is evidence that there is inherent consistency among the dataset. The outlier are not significant in the dataset.

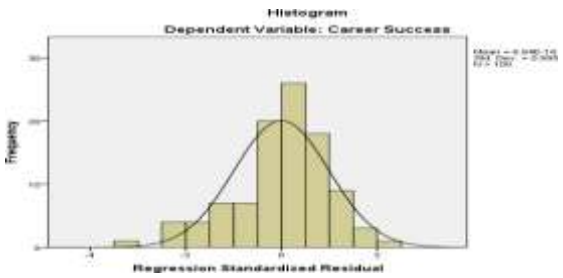


Table 3 - Coefficients[a]

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	2.348	.393		5.972	.000
	Emotional Intelligence	.346	.101	.328	3.443	

a. Dependent Variable: Career Success

Y = a + bX
Y = 2.348 + 0.346 X
Where,
Y = Career Success
X = Emotional Intelligence
a = Constant
b = Intercept

This shows the present dataset evidences that there is positive relationship between career success and emotional intelligence of the target respondents. Where, 'a' is 2.348 and the gradient is 0.346. This clearly indicates higher the emotional intelligence (Independent variable) that results higher career success which proves the assumptions.

Scope for further study

The present study can be extended in various dimensions to understand and integrate how emotional intelligence is closely related to career success. The study has been conceived based on the information collected from mid-level managers, which can be experimented with senior level or even entry-level officers. The study region was concentrated to within the state of Arunachal Pradesh. However, it can be extended to neighboring states or entire north-east India in order to widen the catchment area for data collection. In that case, the outcome of the sampling would be more representative and can comprise of mixed set of variations representing various sectors or industries.

Limitations of the study

The sample size in the present study is 100 mid-level service managers from Arunachal Pradesh. The higher the sample size shall ensure greater precision of the study outcome. The study suffers from the samples belonging to managers from manufacturing unit since the state does not have significant manufacturing establishment.

Conclusion

The present research work has demonstrated that there is positive relationship between emotional intelligence and career success among the mid-level service managers working in the North-Eastern state of Arunachal Pradesh. Emotional intelligence.. The results obtained are inconsonance with other previous studies. This shows that emotional intelligence is still the driving force that can manifest higher career growth even in a small nascent state like Arunachal Pradesh. The outcome of the study may be helpful for the organizations that they may consider and influence the importance of emotional intelligence among the top management for mentoring the subordinate managers for their respective career success.

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An Engineering Approach for Modeling and Design of a Diaphragm Based Comb Drive Capacitive Pressure Sensor

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Abstract: The Microelectromechanical (MEMS) diaphragm based comb drive capacitive pressure sensor has two stages, Mechanical (Diaphragm) and Capacitive (Comb Drive). The diaphragm displaces in response to apply pressure and the displacement moves the movable comb structure. The two most common architectures of comb drive are single side comb structure and double fold comb structure. In this paper, an impressive technique for designing and modelling of single side comb structure capacitive pressure sensor is being presented. A mathematical model of the sensor is derived and the model simulates the designed structure with the COMSOL Multiphysics Simulator. The Mechanical Sensitivity, Electrostatic sensitivity and Overall Sensitivity are studied for the designed structure. A comparative study of the mathematic analytical values and simulated output values are examined and are found very much closed to each other. The various parameter like Young's Modulus, Poisson's Ratio, Dimensions and Structure of the pressure sensor, number of comb fingers and dimension of the comb finger affecting the sensitivity is widely discussed.
Keywords: coupler, fringing effect, electrostatic sensitivity, mechanical sensitivity.

1. Introduction

There are various pressure sensors viz. Piezo-resistive Strain Gauge, Capacitive, Electromagnetic, Piezo-electric, Strain Gauge, Optical, Potentiometric, Resonant, Thermal (Pirani Gauge) and Ionization but few of them are applicable for MEMS design. The advantages of MEMS technology are: small in size, volume and mass, low power consumption, low cost, compatible with silicon technology, low heating effect, parallelism etc. The capacitive pressure sensor is an active sensor as it requires an external power source to operate. It is one of the common in MEMS design. MEMS-based comb drive capacitive pressure sensors are miniaturized, consume less power and more efficient. Such sensors have wide application in the field of pressure monitoring, safety purpose, controlling etc. The capacitive has a wide application in various fields in monitoring, LC tank circuit, high pressure sensing, harsh environment, biomedical, measuring plantar pressure, measuring bowel state, microphone, and ultralow pressure detection [1–10]. Capacitive pressure sensor can be developed with silicon micromachining fabrication technique [11]. Many researchers use ANSYS and COMSOL finite element method multiphysics simulator for simulation [6,12,13]. Some researchers have proposed a diaphragm based comb drive pressure sensor but their study is the effect of different material properties on the sensitivity [14]. In this study, the systematic design approach for comb drive is being studied.

The working principle of comb drive capacitive pressure: the measuring pressure is applied at the mechanical sensing structure, common structures are diaphragm, bridges or cantilever, and deflect. The deflection is coupled with the coupler to translate into linear displacement and displaced the comb position resulting in the changes in capacitance.

2. Sensor Design Structure

In this paper, diaphragm-based comb drives capacitive pressure sensor has four main structures i.e. diaphragm structure, mechanical coupler, movable comb structure and fixed comb structure as is shown in fig1. The diaphragm is the structure where the pressure (stimulus) is applied and converts pressure into deflection or displacement. A square diaphragm with dimension is 200µmX200µmX5µm is considered for the design. Mechanical coupler is to translate the diaphragm deflection into linear displacement and couples to movable comb drive. Since the maximum deflection of the square diaphragm is at the centre, mechanical coupler is connected at the centre of the diaphragm and at the other end movable comb drive. The dimension of the coupler is 6µmX6µmX10µm. A comb structure having ten fingers on both side with a gap of 15µm in between the two fingers. The dimension of a finger is 200µmX40µmX5µm. The length of the finger G_1 is 40µm, the gap between the two plates G_2 is 80µm and the gap between the two adjacent fingers of movable and fixed comb G_3 is 5µm.

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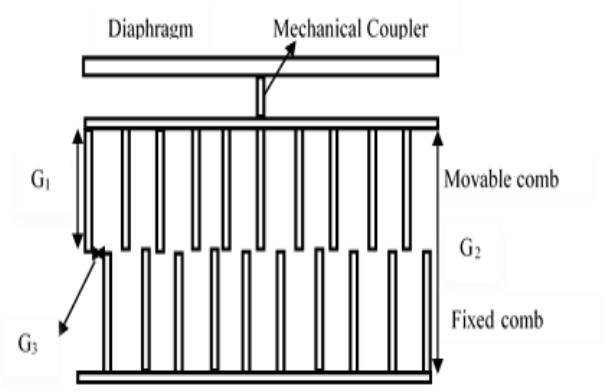

Fig. 1 *Schematic Diagram of Comb Drive.*

3. Mathematical Modelling

The diaphragm based comb drive capacitive pressure sensor has a combination of mechanical and electrostatic. In mechanical modelling, the pressure or force is applied at the diaphragm and deflects the diaphragm. The generalized equation of square diaphragm deflection W is eqn. 1[15,16]. Where, D is the flexure rigidity given by eqn.2.

$$W(x,y)=(0.0213pa^4/D)(1-x^2/a^2)^2(1-y^2/a^2)^2. \quad (1)$$

$$D=Eh^3/(12(1-v^2)). \quad (2)$$

Where,

E: is the Young's Modulus,

h: is the thickness of the diaphragm,

v: is the Poisson's Ratio,

a: is the half length of the square diaphragm,

x,y: is the coordinate of the diaphragm from the centre as an origin.

The maximum deflection occurs at the centre of the diaphragm i.e. x=a, y=a. The maximum deflection is given by eqn.3.

$$W(x,y)_{max} = W(0,0) = pa^4/47D. \quad (3)$$

Mechanical sensitivity, S_M, is given by the ratio of change in deflection to change in the applied pressure. It is given by the eqn.4.

$$S_M = \delta w/\delta p. \quad (4)$$

Where,

δw is the change in deflection with respect to applied change in pressure δp.

The deflection and mechanical sensitivity of the diaphragm depends on many parameters such as Young's modulus, Poisson's Ratio of the materials, length, breadth and thickness of the diaphragm.

3.1. Electrostatic modeling

In electrostatic, the capacitance, C, of a parallel plate capacitor is given by eqn. 5

$$C = \mathcal{E}A/g \quad (5)$$

Where, $\mathcal{E}$ is the relative permittivity, A is the area of the plate and g is the gap between the plates.

To calculate the capacitance value of the comb drive, there are 5 (five) parallel plate capacitances and fringing capacitance, which connected in parallel in a simple comb structure as shown in fig. 2. Parallel plate capacitances C_3, C_4 and C_5 are same value and Capacitance C_1 and C_2 has same value since they have same gabs, area and dielectrics.

The overall parallel plate capacitance, $C_{parallel}$, of the simple comb drive is given by eqn. 6.

$$C_{parallel} = C_1 + C_2 + C_3 + C_4 + C_5 \quad (6)$$

$$C_{parallel} = 2C_1 + 3C_3 \quad (7)$$

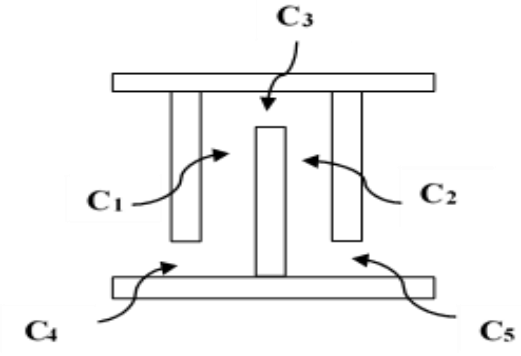

Fig. 2 *Various capacitance in comb drive.*

Considering, the design structure dimensions, the capacitance C_1 and C_3 values will be given by eqn. 8 and eqn. 9 respectively.

$$C_1 = \mathcal{E}l(\delta w)/G_3 \quad (8)$$

$$C_3 = \mathcal{E}tl/(G_1 - \delta w) \quad (9)$$

Where, $\mathcal{E}$ is the relative permittivity, l is the length of the finger, t is the thickness of the finger, G_3 is the gap between the two finger, G_1 is the gap between the tips of the finger and base of the opposite comb and δw is the change in displacement of the finger. N_3 is the total number of fringing area.

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The total capacitance of the design comb drive can be express by eqn. 10.

$$C_{parallel} = N_1C_1 + N_2C_3 \quad (10)$$

The fringing effect capacitance is given by eqn. 11.

$$C_{fringing} = N_3 \mathcal{E}(G_1 - \delta w)l / G_3 \quad (11)$$

$$C_{total} = C_{parllel} + C_{fringing.} \quad (12)$$

The electrostatic sensitivity of the sensor is the sensitivity which is the ration of change in capacitance to change in deflection. It is given by eqn. 13.

$$S_E = \delta C_{total}/\delta w \quad (13)$$

The overall sensitivity is the sensitivity which is the ratio of change in capacitance to change in applied pressure. It is given by eqn.14.

$$S_{Total} = \delta C_{total}/\delta w = (\delta w/\delta p)(\delta C_{total}/\delta w) = S_M S_{E.} \quad (14)$$

The overall sensitivity is equal to the product of mechanical sensitivity and electrostatic sensitivity.

4. FEM Simulation

The proposed 3D meshing model is designed in the COMSOL Multiphysics simulator as it illustrated in the fig.3. The device has ten fingers in each, movable comb drive and fixed comb drive. The material used is gold (Au) from the inbuilt COMSOL material for the fingers and diaphragm. The gap between the combs is filled with air as a dielectric. A voltage of positive one volt is given in the movable plate and ground on the fixed plate. The physics for simulation is Electromechanics (emi) and the study is stationary. The meshing is done with Free Tetrahedral and number of elements is 1164398.

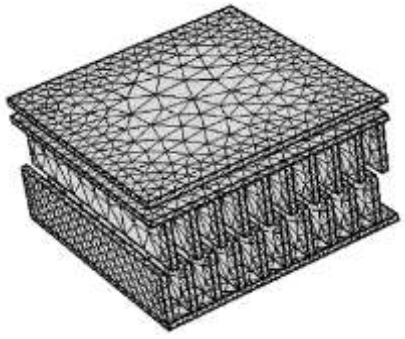

Fig. 3 *Mesh model of comb drive.*

Table 1. Gold (Au) properties.

Properties	Value	Unit
Density	19300	Kgm^{-3}
Young's Modulus	70	GPa
Poisson's Ratio	0.44	1

5. Comparisons of Simulated values and analytical values

Various comparisons are made between the analytical and simulated values. The mathematical model equations are realized in MATLAB and simulation in COMSOL Multiphysics. The graph between the deflections and the applied pressure in Fig. 5 shows linearly varying. The Mechanical Sensitivity (S_M) of the analytical and simulated are 0.023 µm/KPa and 0.020 µm/KPa.

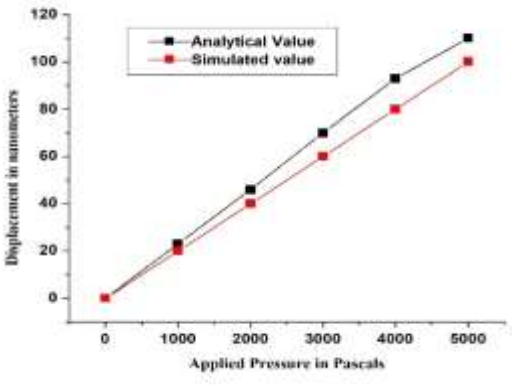

Fig. 5 Applied pressure Vs *Displacement*

The comparison is made between the analytical and simulated value of capacitance for the set of applied pressure in table 2.

Table 2. Analytical and Simulated value of Capacitance for applied pressure.

Applied Pressure (KPa)	Analytical Capacitance (pF)	Simulated Capacitance (pF)
0	0.073413	0.071560
1	0.073430	0.071570
2	0.073447	0.071580
3	0.073464	0.071590
4	0.073481	0.071600
5	0.073498	0.071610

The overall Sensitivity (S_{total}) of analytical and simulated are 0.000017 pF/KPa and 0.000010 pF/KPa respectively. The electrostatic sensitivity (S_E) of analytical and simulated are 0.000739 pF/µm and 0.000500 pF/µm respectively.

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6. Conclusion

From this study, the sensitivity of diaphragm-based comb drive capacitive pressure sensor depends on the material properties and dimension of the diaphragm and the structural design of the comb drive. The capacitance of the sensors is increased linearly with an increase in pressure. For this particular design, the sensitivity is found to be 0.000017 pF/KPa and 0.000010 pF/KPa for analytical and simulation respectively.

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A Novel Design and Modeling of Beam Bridge structure Piezoelectric Pressure Sensor base on ZnO

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Abstract:
The main objective of this study is to design a ZnO base beam bridge MEMS piezoelectric pressure sensor. A theoretical mathematical modeling of the design is derived for the structure. Factor effecting the output or efficiency is studied base on mechanical and electrostatics step by steps. A simulation is conducted on Comsol Multiphysics Simulator for the design for validating the theoretical modeling and a comparative study are made between the analytical and simulated result. This study will help to find the optimum design structure for piezoelectric pressure sensor base on bridge beam structure.

Keywords—Young modulus, Poisson Ratio, deflection,stress, voltage constant

1. Introduction

There are four common principle use for pressure to energy conversion – capacitive, inductive, piezoresistive [1-6] and piezoelectric [7–11]. Among these sensor, piezoelectric base MEMS sensor is a passive sensor as it doesn't require any electrical power excitation. Capacitive, inductive and piezoresistive MEMS sensor are active sensors as they required external power excitation.

Mechanical beam bridge structure is choosing for the study as it provides more stable then the cantilever type. In cantilever the structure is clamped or supported at one end whereas bridge beam structure is provides clamped or support at opposite two ends. In mechanical bridge beam structure or cantilever structure the maximum stress is occur at the edges of clamped area. The stress is directly proportional to charge developed on the surface of piezoelectric material. So in thisbeam structures the sensing material can be put at both the opposite edge.

Zinc Oxide (ZnO) is used for this study as it is widely available, low cost and most common material used in the research and industrial. ZnO has also wide application in the field of semiconductor and photo conductivity. It also has a high voltage constant. It hasthermochromicsproperties i.e. change in colour when heated from white to yellow, and when cooled down the colour back again to white colour because of various types of crystal lattice defects [12].

2. Illustrations

2.1. Mechanical Modeling

In this modeling, the applied pressure are converted into mechanical properties like deflection and stress. The basic theoretical differential equation of the beam was introducedin [13][14]. Let us consider for the coordinate system for a bridge beam structure as in Fig. 1.

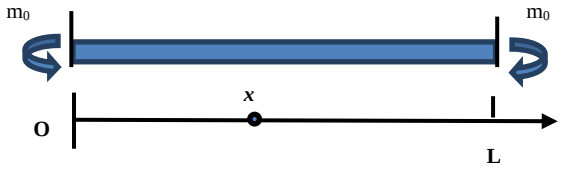

Figure 1: Structure of Bridge.

The governing mathematical expression of the equation is

$$-EIw''(x) = Fx/2 - Fx^2/2L - m_0, \quad (1)$$

where,*E* is Young's Modulus of the beam material, *I* is the moment of inertia of the structure, $w''(x)$ is the second derivative of the deflection for the beam at position *x*, F is the uniform force applied on the surface,*x* is the position on the beam, L is the length of the beam and m_0 is the moment on the clamped.

Equation (1) is integrated with respect to *x* and can be written as follow

$$-EIw'(x) = Fx^2/4 - Fx^3/6L - m_0x. \quad (2)$$

Putting the boundary on $w'(L) = 0$, the value of

$$m_0 = FL/12. \quad (3)$$

Equation (2) is integrated with respect to *x* and after putting the value of

m_0. The equation can be written as follow

$$-EIw(x) = Fx^3/12 - Fx^4/24L - FLx^2/24, \quad (4)$$

Or

$$w(x) = Fx^2(L-x)^2/(24ELI). \quad (5)$$

Equation (5) gives the deflection $w(x)$ of the beam at position *x*. The maximum deflection is occur at the centre of the beam i.e. *x* = (L/2) so, the maximum deflection equation is given as follow

$$W_{max} = FL^3/(384EI). \quad (6)$$

The moment of inertia for the rectangular beam type given by the following equation

$$I = bh^3/12 \quad (7)$$

Equation (6) can be written after putting the value of *I* as follow

$$W_{max} = FL^3/(32Ebh^3). \quad (8)$$

The stress on the beam is given by the following expression

$$T(x) = -Ezw''(x). \quad (9)$$

Where, *z* is the distance from natural plain i.e. $z_0$of the beam. Natural plain is the plain where minimum stress has been occur in the geometry,when pressure is applied on the structure. Generally, it is the mid plain of the beam for single layer.

Equation (1) can be written after putting the value of m_0 and *I* on (9),

$$T(x) = zF(6x^2 - 6xL + L^2)/ bh^3L. \quad (10)$$

For single layer the maximum stress is occur at *x* = *L* and *x* = 0 on the top of the surface i.e. for single layer *z* = *h/2*. Equation (10) can be rewritten as follow

$$T_{max} = FL/2bh^2. \quad (11)$$

For multiple layers geometry have different layers like silicon layer, silicon dioxide, metal electrode and sensing layer etc. In such case the value of *z* is depend on the natural plain i.e. z_0.

Consider a multi-layer composite system as in fig. 2. In [13], the natural plain position can be determine by the following equation

$$z_0 = (E_1 t_1 (z_1+0)+E_2 t_2 (z_2+z_1)+\ldots+E_n t_n(z_n+z_{(n-1)}))/(2(E_1 t_1+E_2 t_2+\ldots+E_n t_n) \quad (12)$$

Where, $E_1, E_2 \ldots E_n$ are the Young's modulus of the layers for the layers with $t_1, t_2 \ldots t_n$ are the thickness of the layers respectively. And the value of $z_n$is given by the following formula

$$z_n = \sum_{j=1}^{n} t_j, \quad (13)$$

where, i = 1, 2, 3, 4, … n.

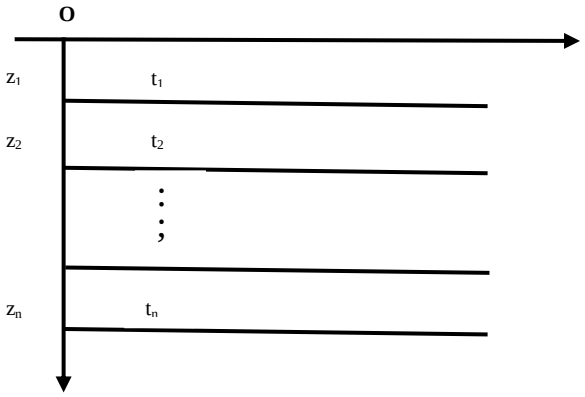

Figure 2:multi-layer composite system.

2.2 Electroststic Modeling

In [15], the conversion of mechanical stress to electrostatic charge for ZnO piezoelectric is given by the following expression

$$q(x) = T(x)d_{31}, \quad (14)$$

where, d_{31} is the strain constant of ZnO, q(x) is the total charge developed on the surface.

For the conversion of mechanical stress to electrostatic voltage is given by the following expression

$$V(x) = T(x)tg_{31}, \quad (15)$$

where, g_{31} is the voltage constant of ZnO, V(x) is the voltage developed between the surfaces and t is the thickness of the piezoelectric.

3. Design model and simulation

A model has been design for prediction in the Comsol Multi-Physics Simulator. In simulation, the physics used is Electromechanical and the study is Stationary. Here, a bridge consisting of Silicon (Si) layer as mechanical structure, Silicon-dioxide (SiO_2) layers as insulator between Si and electrodes, Gold (Au) as electrodes and ZnO layer piezoelectric is consider as shown infig. 3. The dimensions of the each layers are tabulated in table no. 1

Table 1: Dimension and Properties used in design.

Parameters	Symbols	Value	Unit
Dimension of Si	$(L \times B \times T)_1$	300x50x10	µm³
Dimension of SiO_2	$(L \times B \times T)_2$	300x50x3	µm³
Parameters	**Symbols**	**Value**	**Unit**
Dimension of Au	$(L \times B \times T)_3$	50x50x1	µm³

Dimension of ZnO	**(L x B x T)4**	**50x50x5**	**µm3**
Young's Modulus of Si	**E1**	**160**	**GPa**
Young's Modulus of SiO_2	**E2**	**70**	**GPa**
Young's Modulus of Au	**E3**	**70**	**GPa**
Young's Modulus of ZnO	**E4**	**120**	**GPa**
Strain Constant of ZnO	**d_{31}**	**-5.43×10^{-12}**	**m/V**
Voltage Constant of ZnO	**g_{31}**	**-4.85×10^{-2}**	**Vm/N**
Applied Pressure	**p0**	**200**	**Pa**

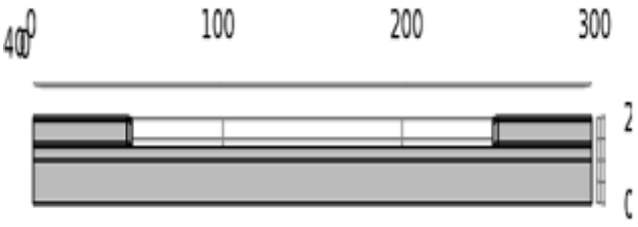

Figure 3:Design Structure

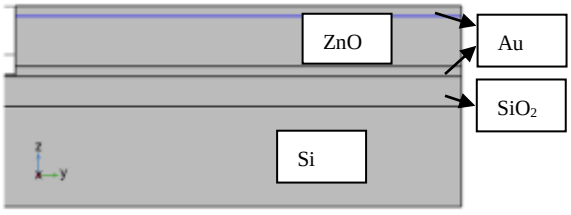

Figure 4:Multilayer in sensing area

4. Simulation Output

4.1 Deflection and Stress

In mechanical design, the deflection and the stress is an important parameters for study. As the maximum deflection is occurs at mid of the bridge but the maximum stress is occur at the edges on the ends of the bridge. As from the deflection output as shown in fig. 5 the maximum deflection is occur at the centre of the bridge.

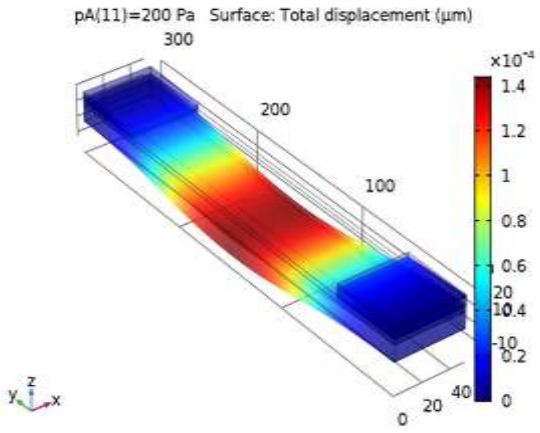

Figure 5: Simulation output showing maximum deflection at the center.

The analytical deflection value and simulated deflection value with different applied pressure is tabulated as in table 2.

Table 2: Pressure Vs Maximum deflection for analytical and simulated.

Sl. No.	Pressure Vs Maximum Deflection		
	Applied Pressure [Pa]	***Analytical [µm]***	***Simulated [µm]***
1	0	0	0
2	20	1.440E-5	1.436E-5
3	40	2.880E-5	2.871E-5
4	60	4.320E-5	4.303E-5
6	80	5.760E-5	5.732E-5
7	100	7.200E-5	7.147E-5
8	120	8.641E-5	8.623E-5
9	140	10.081E-5	10.001E-5
10	160	11.521E-5	11.483E-5
11	180	12.962E-5	12.901E-5
12	200	14.402E-5	14.362E-5

But for the stress, the maximum stress is occur at the edges of the joint as shown in fig. 6.

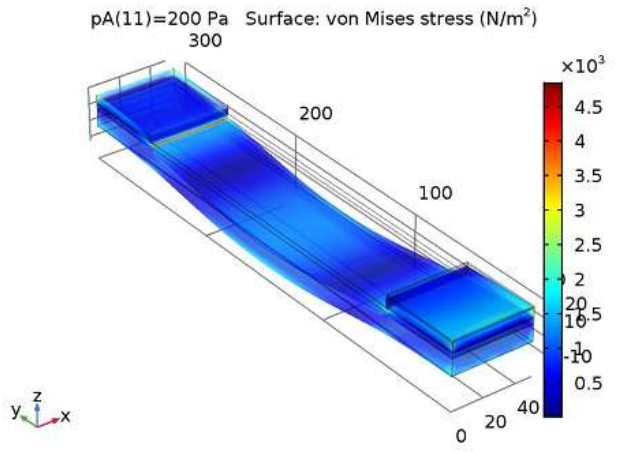

Figure 6: simulation output showing maximum stress at the edges.

The analytical maximum stress value and simulated stress value are tabulated as in table 3.

Table 3: Pressure vs Maximum Stress for analytical and simulated.

Sl. No.	Pressure Vs Maximum Stress		
	Applied Pressure [Pa]	***Analytical [N/m²]***	***Simulated [N/m²]***
1	0	0	0
2	20	2250	2363
3	40	4500	4778
4	60	6750	7162
6	80	9000	9813
7	100	11250	12099
8	120	13500	14767
9	140	15750	16720
10	160	18000	19593
11	180	20250	21744
12	200	22500	24662

In electrostatic design, the potential difference across the upper layer and lower layer of the piezoelectric material is studied. The potential voltage is developed due to the charge is developed due to the stress induced on the sensing material. The developed surface voltage is directly proportional to the pressured or force applied on the material. The simulation output is showing the potential developed at applied pressure as in fig.7.

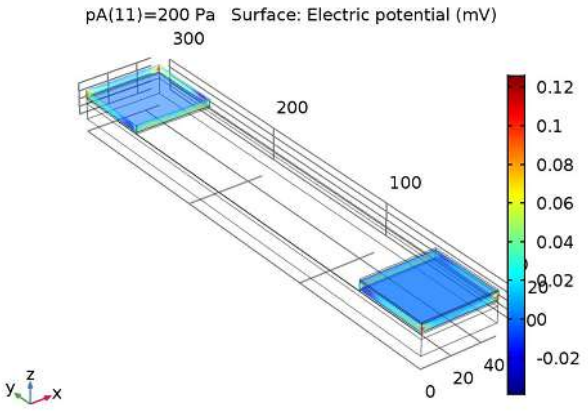

Figure 7: Simulation output is showing the potential developed.

The analytical potential difference value and simulated potential difference value are tabulated as in table 4.

Table 4: Pressure Vs Potential Differences.

Sl. No.	Pressure Vs Potential Differences		
	Applied Pressure [Pa]	***Analytical [mV]***	***Simulated [mV]***
1	0	0	0
2	20	0.0909	.09107
3	40	0.1819	0.2298
4	60	0.2728	0.3271
6	80	0.3637	0.3943
7	100	0.4547	0.4928
8	120	0.5456	0.59145
9	140	0.6366	0.6900
10	160	0.7275	0.7886
11	180	0.8184	0.8871
12	200	0.9094	0.9785

5. Discussion and Conclusions

A theoretical modeling approach for design piezoelectric beam bridge pressure sensorhas established and validate by using Comsol Multiphysics simulator. As the simulated output and analytical output of

the very close, this design process can be implemented for designing the ZnO piezoelectric beam bridge pressure. This design process can be implemented for optimizing of the sensor too. The various factor affecting the sensitivity are applied pressure, dimension of the sensor structure, Young'smodulus (E), Poison's ratio (v) and the voltage constant (g_{31}). The sensitivity is also affected by the material used in the multilayer structure since the Young's modulus and Poison's ration has different value for different material. The ZnO is used because it has high voltage constant. The mechanical sensitivity of the deflection to applied pressure and stress to applied pressure are 0.071µm/Pa and 118 N/m^{2}Pa respectively. The electrostatic sensitivity or the overall sensitivity of the sensor is 0.00489 mV/Pa. This designed sensor can be implemented for low pressure sensor as the sensitivity is very high.

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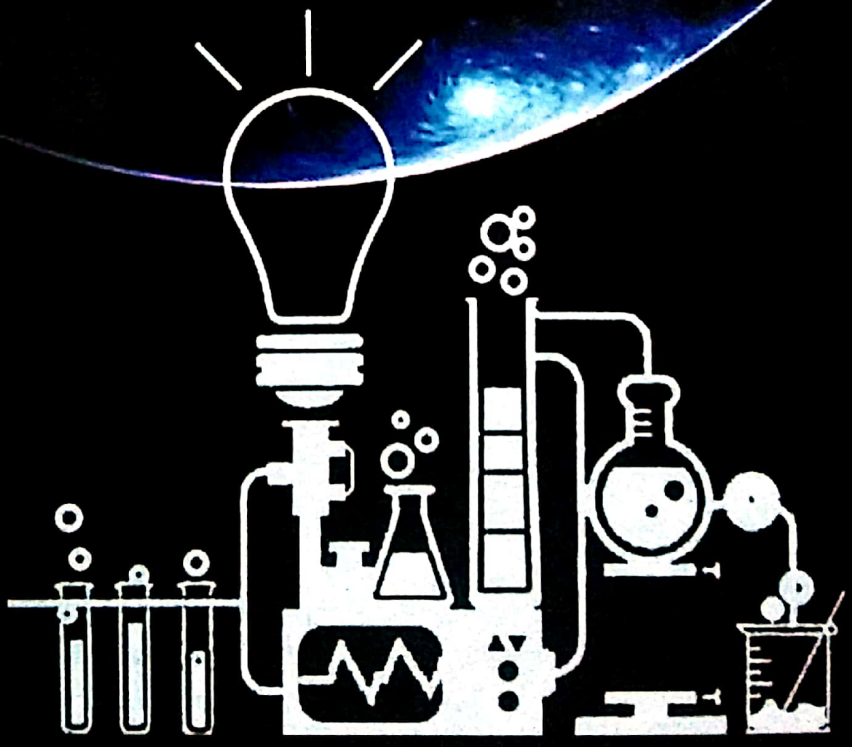

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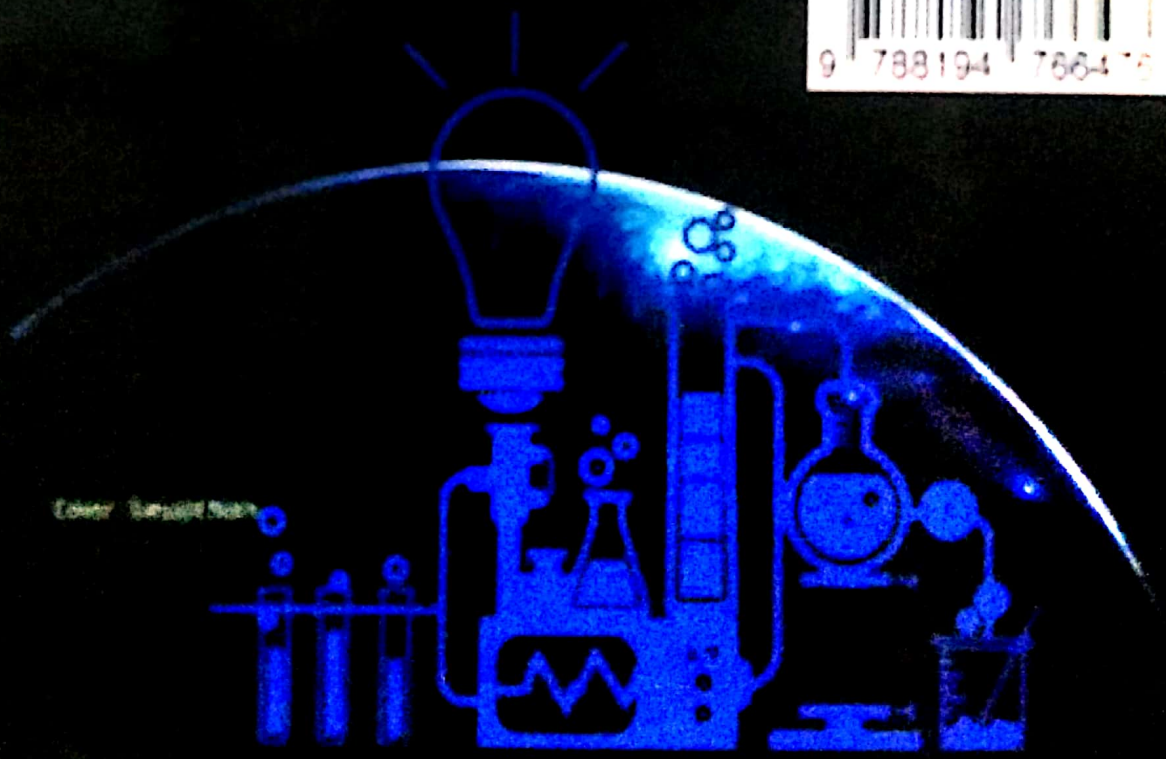

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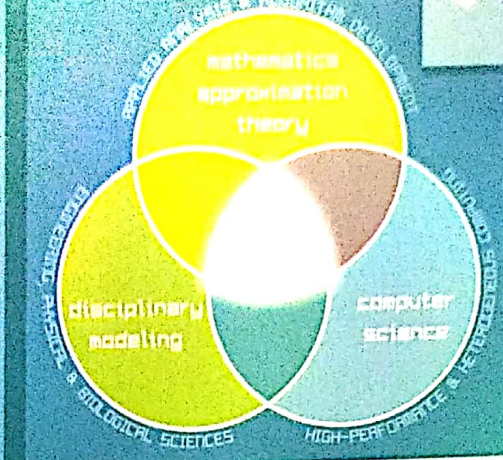

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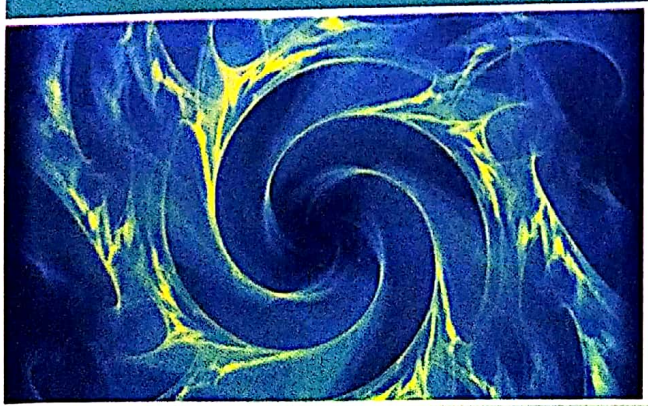

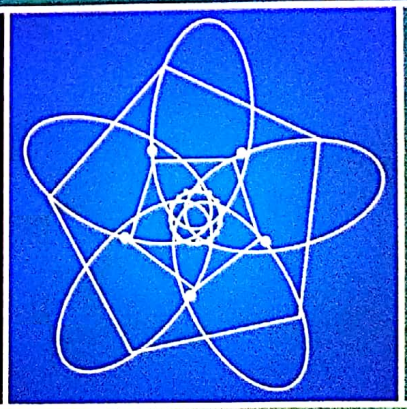

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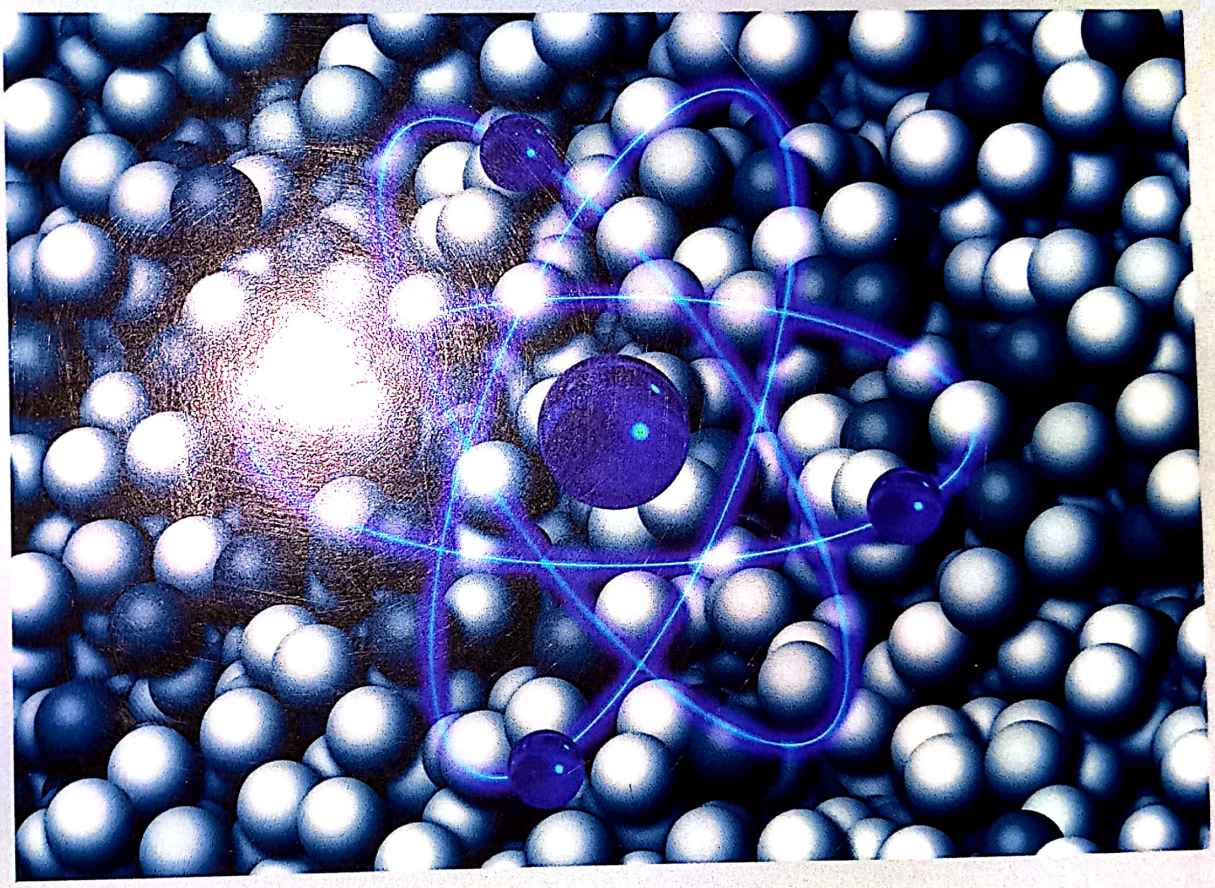

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Synthesis and Characterization of CdS/PbS Core-shell Nanocomposites for Photovoltaic Application

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Y. Nanung
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P. K. Kalita

Abstract

CdS/PbS core shell has been synthesized through chemical route.CdS shows hexagonal whereas PbS shows cubic structure. The absorption and photoluminescence studies show a red shift of absorption edge and near band gap emission of core CdS when coated with shell PbS. CdS shows bandgap 2.7 eV and PbS 2.2 eV whereas the CdS/PbS nanocomposites show a bandgap of 2.3 eV. The optical properties clearly signify the formation of quasi type II CdS/PbS core shell nanocomposites that can be used for photovoltaic devices.

Keywords: *CdS/PbS core shell, exciton, blue shift, photoluminescence.*

Introduction

Semiconductor nanostructures especially the core-shell nanocomposites have been attracting a tremendous interest owing to their huge possible application in optoelectronic and photovoltaic devices due to their outstanding optical and electrical properties[1-9]. With this motive one cannot ruled out the role of II-VI semiconductors as the mentioned properties of these materials are strongly dependent on their size and structural morphology which are easily tunable at

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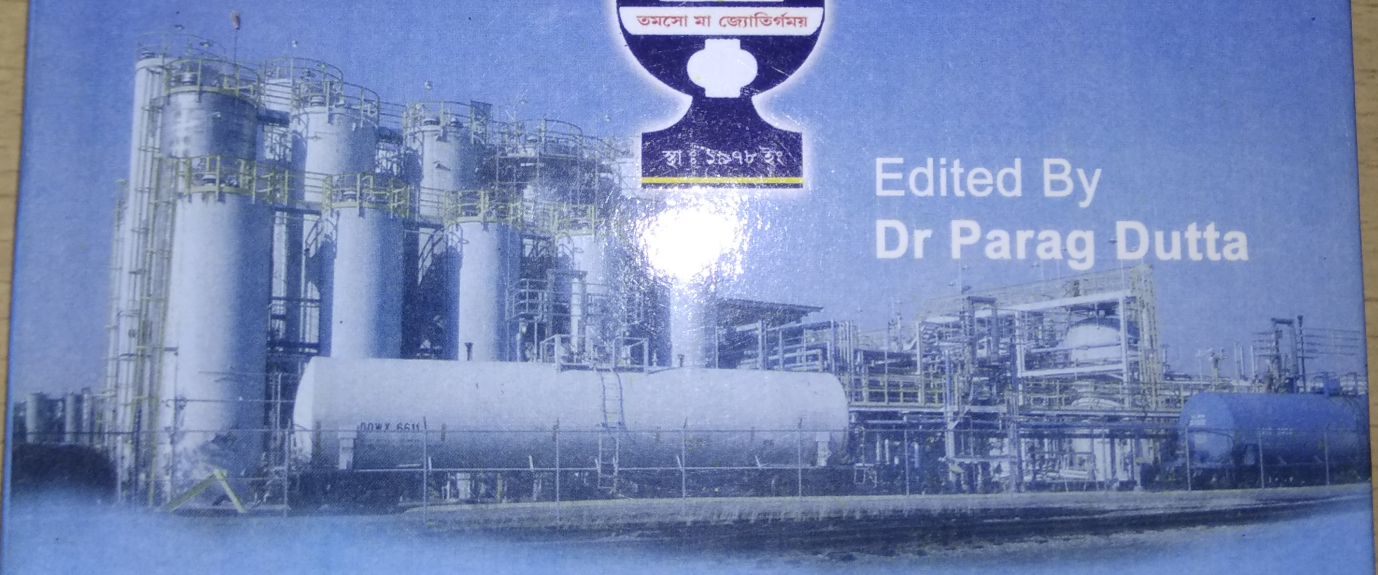

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Unorganised Sector Enterprises and Assam Economy

Dr Prasenjit Bujar Baruah*

Abstract

The unorganised sector is no longer viewed as a mere transitory phenomenon in the process an economy transforming from an underdeveloped to a developed one. This sector, which is now recognised as a characteristic feature of the developing economies, provides livelihood to a disproportionately large number of households in developing countries. In those countries, this sector has been playing an important role both in terms of employment generation and contribution to gross domestic product. Assam is one of the relatively backward states in India; where the unorganised sector is expected to play an important role. This paper based on secondary data compiled from different rounds of national sample survey reports tries to analyse the role of nonfarm unorganised sector enterprises in Assam economy.

JEL Classification: E26 and J46

Dr Prasenjit Bujar Baruah, Assistant Professor, Department of Economics, Rajib Gandhi University, Arunachal Pradesh

Education at the Crossroads

New Thoughts of the Changing Era

Editor

Dr. Amitabh Roy

This collection of 22 essays focus on the much-discussed issues related to the educational scenario today. With the first-hand experience of 'digital divide' of the remotest district of West Bengal, we are well equipped to address the situation from perspectives, not noticed before. Variety of issues have been discussed, lot more need to be focused upon too. But the need of the hour is well addressed in this critical book.

A multi-disciplinary analytical approach has been adopted while discussing the issues related to digital pedagogy and transformation of traditional classroom teaching. A new era is knocking at our door, only need is to respond with critical insight. The barriers are necessary to point out, so that immediate measures can be taken to smoothen the journey towards an exemplified digital education system.

This book will serve as a handbook of new thoughts about education of this new era. Researchers as well as students will be benefitted from the well-chosen essays on the challenges, globally faced by all.

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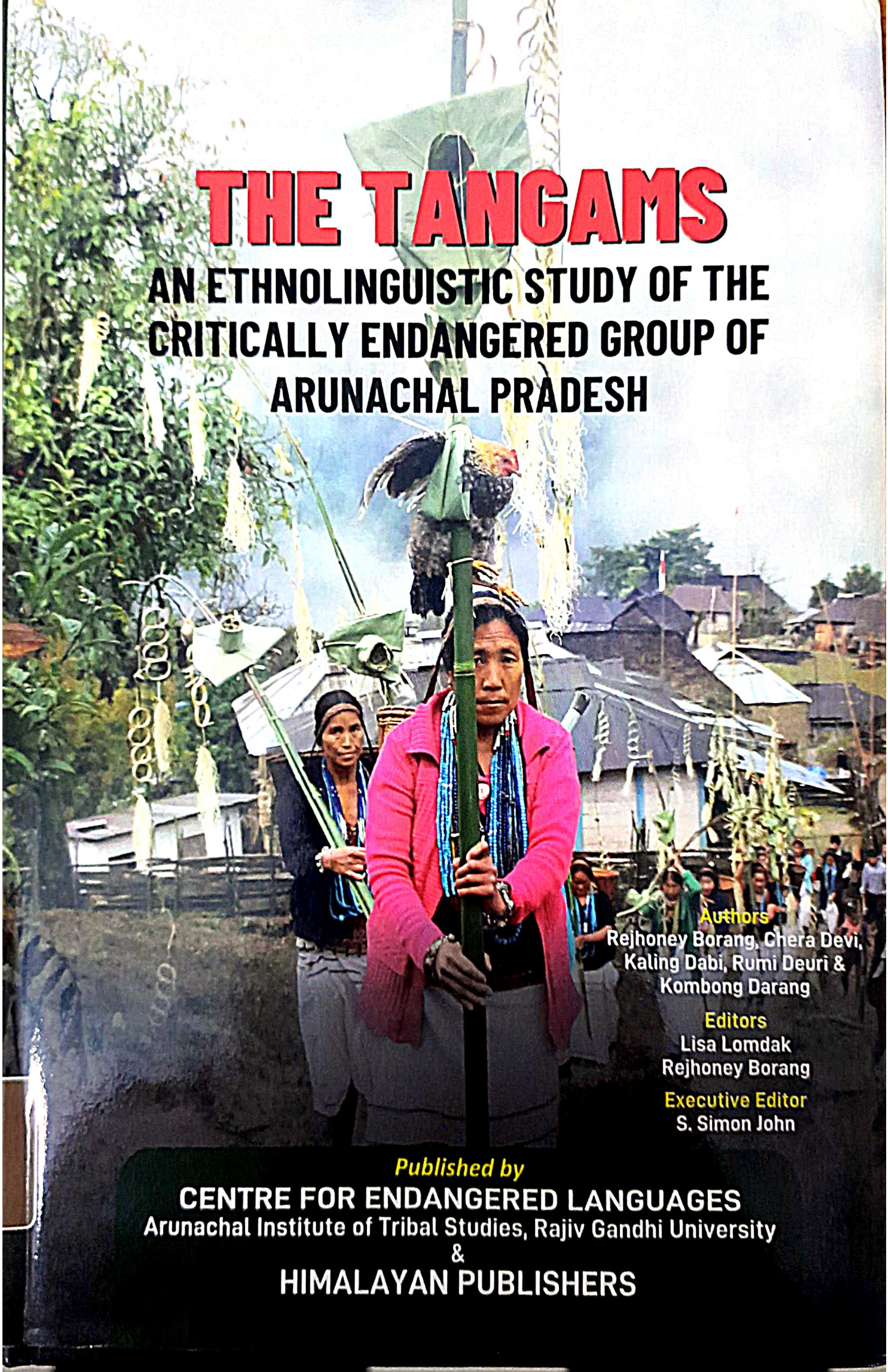
Digital Education to Strengthen the Learning Gaps during New Normal Situation in India

Prasanta Kumar Barik

Introduction

The new normal situation during COVID-19 propelled the use of contactless digital technology across India. Indian used the COVID-19 opportunity to further spread the use of digital technology. An important role was played by Digital India Vision of the Government of India which seems to be an instrument in solving the situation in the present scenario, where every sector is caught in a crisis because of COVID-19. All the sectors including business activities have been put to halt. It has badly affected the education sector too. Educational institutions are shut down and as a result, it is putting a lot of stress on students and youths for their education, admission to career-making courses, skill enhancement, employment opportunities, etc. As, per UNESCO, it has been observed that approximately 157 crore students across the globe are facing a do-or-die situation in terms of education.

This new normal situation during COVID-19 has forced us to re-plan and re-organise our education system within these five to six months. Every one of us is realising that the education system needs to change. Now the policymakers and the educationists need to think seriously about its systematic change. This new normal situation has allowed adopting digital technology in education. It



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AN ETHNOLINGUISTIC STUDY OF THE CRITICALLY ENDANGERED GROUP OF ARUNACHAL PRADESH

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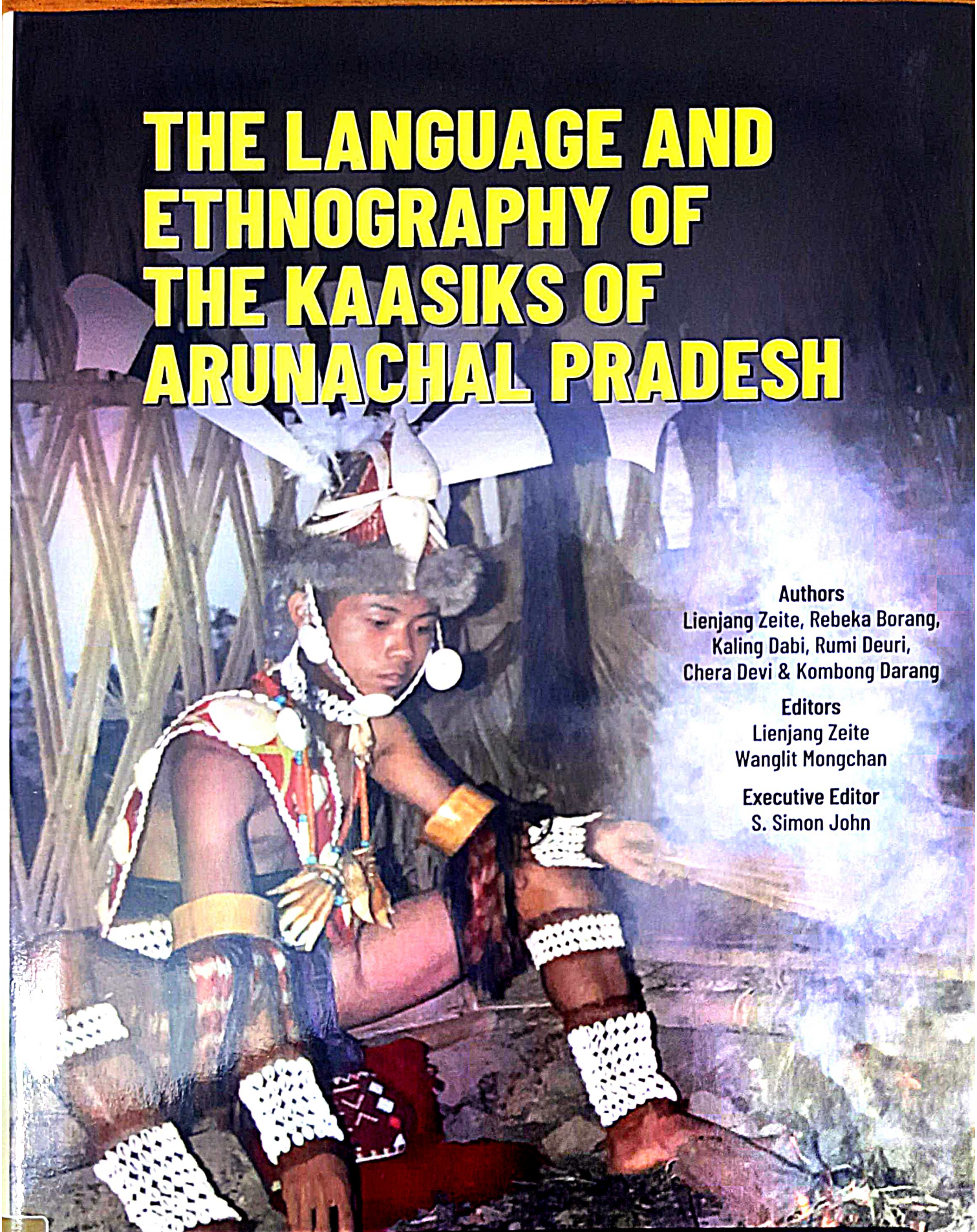

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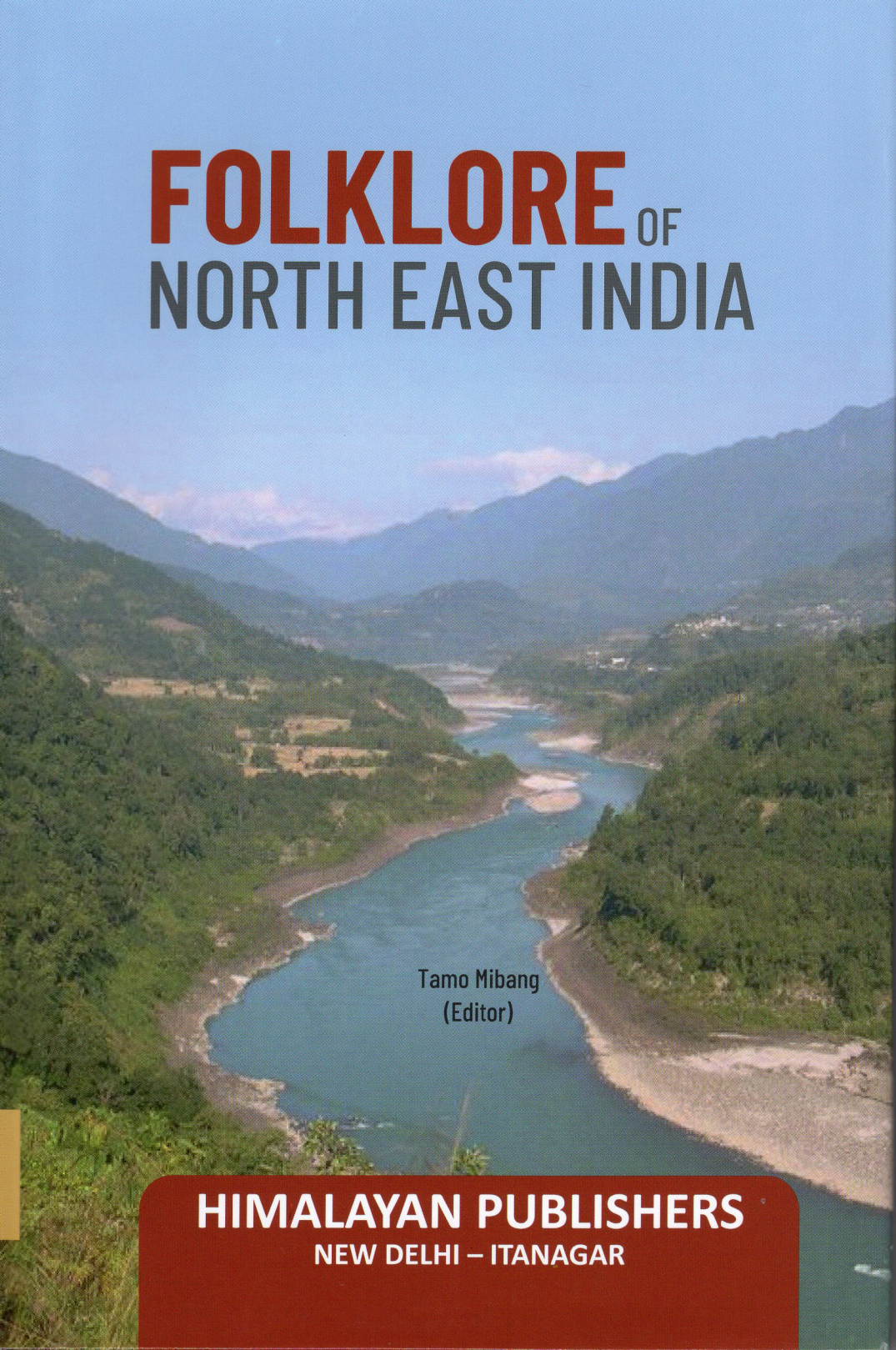

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Preface

The 4th International Conference on Research in Intelligent and Computing in Engineering, popularly known as RICE 2019, was held on August 08–09, 2019 in Hanoi University of Industry (HaUI), Hanoi, Vietnam.

The Fourth edition of RICE 2019, organized by the Electronic Engineering Faculty of the HaUI, provides an international forum which brings together the researchers as well as the industry practitioners, who are actively involved in the research in fields of intelligent computing, data science, or any other emerging trends related to the theme covered by this conference. RICE 2019 provided an opportunity to account state-of-the-art works, to exchange ideas with other researchers, and to gather knowledge on advancements in informatics and intelligent systems, technologies, and applications.

This conference has technical paper sessions, invited talks, and panels organized around the relevant theme. RICE 2019 was the event where the author had the opportunity to meet some leading researchers, to learn about some innovative research ideas and developments around the world, and to become familiar with emerging trends in Science and Technology.

RICE 2019 received a huge response in terms of submission of papers across the countries. RICE 2019 received papers from various countries outside Vietnam such as India, China, Russia, Australia, New Zealand, and many more. The Organizing Committee of RICE 2019 constituted a strong international program committee for reviewing papers. A double-blind review process has been adopted. The decision system adopted by EasyChair has been employed and 118 papers have been selected after a thorough double-blind review process. The proceedings of the conference will be published as one volume in Advances in Intelligent Systems and Computing, Springer, indexed by ISI Proceedings, EI-Compendex, DBLP, SCOPUS, Google Scholar, and Springerlink.

We convey our sincere gratitude to the authority of Springer for providing the opportunity to publish the proceedings of RICE 2019.

To realize this conference in 2019, we really appreciate Hanoi University of Industry to host the conference and to be continuously supporting the organization team during the preparation as well as 2 days of the conference. In addition, we

would like to give a special thanks to Vintech City, a member of Vingroup, that has supported the conference as a diamond sponsor. We would also like to thank the financial support of ASIC Technologies to RICE 2019. Without their support, this conference would have not been successful as the first time being held in Vietnam.

Our sincere gratitude to all keynote address presenters, invited speakers, session chairs, and high officials in India and Vietnam for their gracious presence in the campus on the occasion.

We would like to thank the keynote speaker as Prof. Vijender Kumar Solanki, CMR Institute of Technology, Hyderabad, TS, India; Dr. Le Hoang Son, VNU, Hanoi Vietnam; Dr. Kumbesan, Australia; Dr. P K Pttanaik, KIIT Bhubaneswar, Odisha, India; Dr. Rashmi Agarwal, MRIIS, Haryana, India for giving their excellent knowledge in the conference.

We would like to thank the reviewers for completing a big reviewing task in a short span of time.

We would also like submit our sincere thanks to the program committee members such as Dr. Le Van Thai, Dr. Hoang Manh Kha, Dr. Nguyen Thi Dieu Linh, Dr. Phan Thi Thu Hang, Dr. Tong Van Luyen—Electronic Engineering Faculty of the HaUI; Prof. Tran Duc Tan—Phenikaa University, Vietnam; and Dr. Raghvendra Kumar, GIET University, Gunupur, Odisha, India for their efforts to make congress success.

Moreover, we would like to thank all the authors who submitted papers to RICE 2019 and made a high-quality technical program possible. Finally, we acknowledge the support received from the faculty members, scholars of Electronic Engineering Faculty of the HaUI, officers, staffs, and the authority of Hanoi University of Industry.

We hope that the articles will be useful for the researchers who are pursuing research in the field of computer science, information technology, and related areas. Practicing technologists would also find this volume to be a good source of reference.

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Contents

Health-Care Paradigm and Classification in IoT Ecosystem Using Big Data Analytics: An Analytical Survey

Riya Biswas, Souvik Pal, Bikramjit Sarkar and Arindam Chakrabarty

Abstract The Indian healthcare system is in a dilapidated state. Healthcare is important to society because people get ill. Healthcare is defined as the diagnosis, treatment, prevention and management of disease, illness and preservation of physical and mental well-being in humans. In our paper we have done healthcare surveys to analyze the aspects. In this paper some aspects of IoT healthcare and big data analytics are discussed Big data can be used for better health planning. It's methodology can be used for healthcare data analytics which helps in better decision making. IoT is the fast developing wireless and web technologies sensors are used to predict the disease supported on IoT are used to develop the healthcare sector. Hence it is assertive that we do, various classifications in IOT are discussed. Hence it is assertive that we do initial surveys on the concept of Big Data, on Healthcare aspects and IoT ecosystem as how we can manage to handle large data files.

Keywords Big data · IoT · Healthcare device · IoT ecosystems

1 Introduction

Cumbrous amount of structured and unstructured data it is used to describe by Big data which is a buzzword. Some characteristics of Big data [1, 2]. As healthcare sector is expanding extremely. The volume of produced data is rapidly expanding every year

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due to existence of unique technologies, appliance and transmission [3]. In the current analysis of smart phones and wearable devices, endless figure of health data folder of patient from various challenges continue featured by healthcare industry [4]. Mostly complication arise where system proceed through divergent data sets [5, 6]. Various aspects of IoT is being discussed in this paper i.e Cancer which is a unchecked expansion unusual unit in any place in a body. Heart disease which is a dominating to conditions to that action area that influenced our heart and affect diminish or clog blood vessels. HIV/AIDS is a germ that mark and alter exempt system. Asthma is one of the most common chronic diseases that has a intelligent impact on people's well-being and in our society. Diabetes is a scheme of metabolic diseases consist of high blood sugar levels concluded lengthy season. For tracking the disease IoT are implemented. IOT basically a model for interconnecting sensor which track, sensing, process and diagnosis [7]. IOT basically composite of physical objects and domain where enclosed device content across the internet [8, 9]. IoT assist self management of disease. Over internet areas like health, Logistics, industry, security, agriculture and environment etc are basically empowered by the IOT appliances [10].

In this paper, we are going to discuss literature survey and classification in the Sect. 2. Section 3 deals with the analytical survey, table and policy design

1.1 Motivation

Big data is not only data it has turn into a entire subject, which involves different device, approach and scheme. Big data is transformative attempt in day-day-life. As in present day there is immense bulk of data, examining these acceptable sets which encompass of structure and unstructured data of various type and size; big data analytics grant the user to evaluate the impractical data to generate a faster and superior judgment. It is establish that big data is calculated to expanding rapidly in healthcare than in other sectors like manufacturing, financial services or media. Big Data and Analytics as with the Internet of Things (IoT). The term big data is one of burning technology. The big data analytics in healthcare covers assimilation and investigation of huge amount of data of complicated heterogeneous data. since Big Data can be advantage to consider user data and the prescribed assistance. It will trying to design program that will allow health care to reach those area where access to hospital was somewhat limited. IoT refers to the computerized intelligent curb and direction of connected associated devices over boundless regions via sensors and other computing capacity.

2 Classification and Analytical Survey

In this section, we will discuss the IoT-based healthcare paradigm and its classification. We have also discussed the analytical survey in this related field.

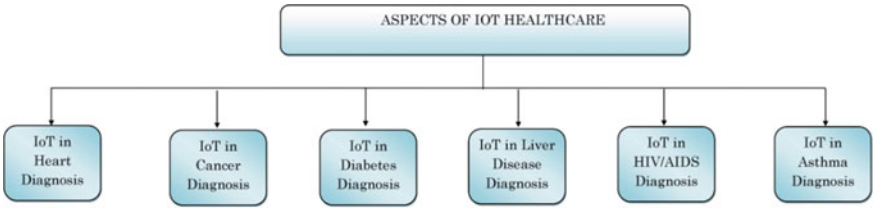

Fig. 1 Classification of IoT aspects

Figure 1 describes the different aspects of IoT-based healthcare. Chavan et al. [9] discussed for creating, acquiring, comparing some technologies like Hadoop, HDFS, Map Reduce, Pig, Hive, HBase are used here. Khan et al. [11] It describes proposed data life cycle which utilize the technologies and nomenclature of Big data management, investigating and scarceness. Nizam et al. [12] discussed that Big data is a type of dataset which is very massive and complicated that get difficultly to computing them exploiting traditional data processing applications. Chen et al. [13] discussed Big data then study about the connected technologies i.e. cloud computing, Internet Of Things, data centers and Hadoop. Archenaa et al. [14] deliver about the perception of how we expose newly expose surplus. Prasad et al. [15] author discussed that diabetes is one of the leading non-communicable disease. This system will prophesy exploring algorithm in Hadoop/Map Reduce environment. Huzooree et al. [16] author explains that Diabetes Mellitus (DM) is one of the starring health hindrance about the world initiating national economical concern. King et al. [17] author discussed that the asthma is characterized by hyper-responsiveness and can be avert by convenient benefit of remedial assistant to conduct asthma charge. Alpert et al. [18] author discussed that the heart failure is an developing public health complication with huge morbidity and probity. Stewart et al. [19] author describes the cardiovascular disease is a compelling and constantly-developing complication. Simon et al. [20] author describes that the HIV-1 pandemic is a complex blend of distinct contiguous. This paper brings on epidemiology. Bhatti et al. [21] author describes that the exploration of the human immunodeficiency virus (HIV) as the original organism of captured immunodeficiency disorder (AIDS). Constatine et al. [10] the author described that breast cancer is one of the biggest fatal disease of world. This paper proposed machine learning algorithm that for Big data analysis leading of an map reduce and mahout. Priya et al. [22] author describes that in first phase, min max normalization algorithm is enforced. Second phase by need of pso character choice. In fourth phase the efficiency will be determined accepting root men square value. Nahar et al. [23] initial forecast of liver disease is very crucial to deliver life and holding appropriate step to curb the disease. Shandilya et al. [24] in the current age automation medical field has develop into one of the favored affair of researcher and cancer. This paper generate survey of such current research study that cause usage of online and offline data for cancer classification. Alharam et al. [25] author describes. The main aim of this paper is for conserving healthcare industry from attack of cyber. Kumar et al. [26] author describes that traditional health center based

approach healthcare is identified with the arrival of large precision sensors and IOT. Kumbi et al. [27] author describes that the IOT is the leading network infrastructure of shipment of connectivity, transportation Technology which is proposed healthcare by the IOT.

3 Analysis of IoT Devices for Healthcare

See Table 1.

4 Policy Design and Constraints in Implementing in India

India seriously needs for reforms in their policy mix particularly in the field of health sector. The world is preparing them to welcome and grab the opportunity matrix that is emerging through the incorporation of 4th Industrial revolution. This is the high time to prepare for optimal participation of Indian firms. The following policy interventions may be exercised.

(i) The 4th Industrial revolution has brought gigantic opportunities in the field of IoT, RFID led ecosystem primarily in the domain of health care sector. The larger enterprises should concentrate in the new business domain as the potential market opportunities are increasing day by day. The big firms or the consortium of large firms may invest on R & D in collaboration with the premier research organizations of the country. The govt. should encourage this mission by offering some lucrative package like tax holiday or relief for the firm for next three years. The firms may be incentivized by promoting SEZ or providing subsidy.

(ii) The Indian MSMEs must initiate to this call of the hour. The firms may introduce their activities in the healthcare domain. As of now, there are various attempts are made to develop innovative branch of research augmenting various forms of technology with the healthcare domain. The branch of biomedical engineering, nano technology and electronic devices is being frequently used in the modern health services. The MSMEs can identify a niche market specializing any of the innovative techno-oriented direction and cutting-edge research which can be converged in modern medical system.

(iii) The IoT based infrastructure can be conjugated with creating healthcare alarming devices. The psycho social behavioral pattern of a set of patients may be studied and the common patterns may be digitally incepted in the IoT led instruments in the line of censory device like e-nose, RFID censors for detecting aroma or pigments and even the unnatural body movements to detect the cases that comes under broader domain of ergonomics.

Table 1 Features and benefits of IoT devices For healthcare

Sl. No.	Disease	IoT devices	Features of IoT device	Benefits
1	Cancer	1. Electronic-nose 2. Biosensor	1. Smart device, authentic, flexibility, quality control 2. Quick, authenticate detection, decent, observing of angiogenesis, cancer metastasis	1. The give off breath of patients with lung cancer characteristics that can be with a computerized nose 2. Biosensors can catch whether a tumor is exist, whether it is favorable or cancerous
2	Heart disease	1. Smartphone 2. Heart beat sensor	1. Rapid analysis, flat cost, familiar 2. Low-cost	1. The sensor associate to a module in the smart phone over the audio jack 2. Heart attack disclosure using Heart Beat Sensor effort on Photoplethysmography (PPG) art.
3	Diabetes	1. Insulin pump 2. Gluco track	1. Flexibility, predictable, reducing wide fluctuations in blood glucose 2. Pain free, Reading history data, user friendly, easy to read data	1. It is a small, automated device that device that bear insulin continuously all over the day 2. A glucose monitoring home device sensor is used to measure the concentration blood.
4	Liver disease	1. MRI 2. e-nose	1. Images come, approach organ morphology, physiology, functions contrast 2. Alluring, ancient and marginally faucal aroma of the emit breath	1. MRI evaluate liver function, usually expressed via the Child-Pugh score 2. e-nose could be a authentic non-invasive apparatus for characterizing CLD

(continued)

(iv) In the era of big data analytics, the predictive analogy in the healthcare sector is emergent to prevent it mammoth outcome on human civilization. The growing concerns of environmental pollution have been challenging the very existence of our civilization. The IoT based ecosystem may be applied in a less expensive manner to identify whether the region are crossing the vulnerable and critical

Table 1 (continued)

Sl. No.	Disease	IoT devices	Features of IoT device	Benefits
5	HIV	1. Photonic crystal (PC) biosensors 2. Novel BioNanoSensor	1. Rapid, sensitive, 100% efficiency, label-free, 2. Inexpensive, portable, simple, sense gases	1. Biosensors optical detection method for bimolecular, cells, and viruses 2. BNS device that employ automation to identify the existence of the HIV
6	Asthma	1. Bracelet 2. HET wristband	1. Authentic measuring and measure 2. Controlling volatile organic compounds, circulatory humidity and temperature	1. It benefit wearers anticipate a looming asthma attack 2. It is a wearable system that could record framework to forecast asthma attacks

level of pollutants so that appropriate measures can be prescribed. The device may also identify the root causes or epicenter of such pollutants so that the multiple stakeholders can intervene and address the issue.

To implement all such modern techniques, India should progress and contribute in the age of Fourth Industrial Revolution. There are several inherent constraints for its implementation particularly in Indian context.

1. The achievement in this new era of technology needs holistic, inclusive and comprehensive growth in the field of technology, its availability, ease of accessibility, technical knowhow for its use, capacity of investment and overall dynamics of its adaptability in real life practice.
2. The IoT technology is the platform to facilitate the healthcare support but the country desperately requires a basic infrastructural facility for healthcare services. The issues of malnutrition, vaccination, basic sanitation and the most importantly the awareness of people in general etc have been creating the stumbling block to achieve success in the cause of humanity.

5 Conclusion

In this literature survey, big data and its various concepts are included. The words big data has been coined to depict this newness. This paper also defines the characteristics of big data. With the advance of big data, we could answer questions that were beyond research in the past, extract knowledge and insight from data. it is understood that

every big data platform has its individual focus. Big data analytics in healthcare is germinating into a promising field for affording acumen from very large data sets and enhancing conclusion while compressing amount. Big Data today carry a lot of promise for the healthcare sector. So, implementing healthcare analytics with expeditious organization, and evolution of big data will make rapid and exact diagnosis which will decrease blunder and bring convenient treatment. using. IoT devices to handle their health requirements. To afford relevant cure to the patient, symptoms are determined from the excessive number of data. Aspects of IoT have been presented.

IoT can detect, determine, and accessed by devices like actuators, sensors or other smart devices. In this paper a review on big data, healthcare, IoT usage in healthcare has been presented.

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इलेक्ट्रॉनिक मीडिया

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अनुक्रमणिका

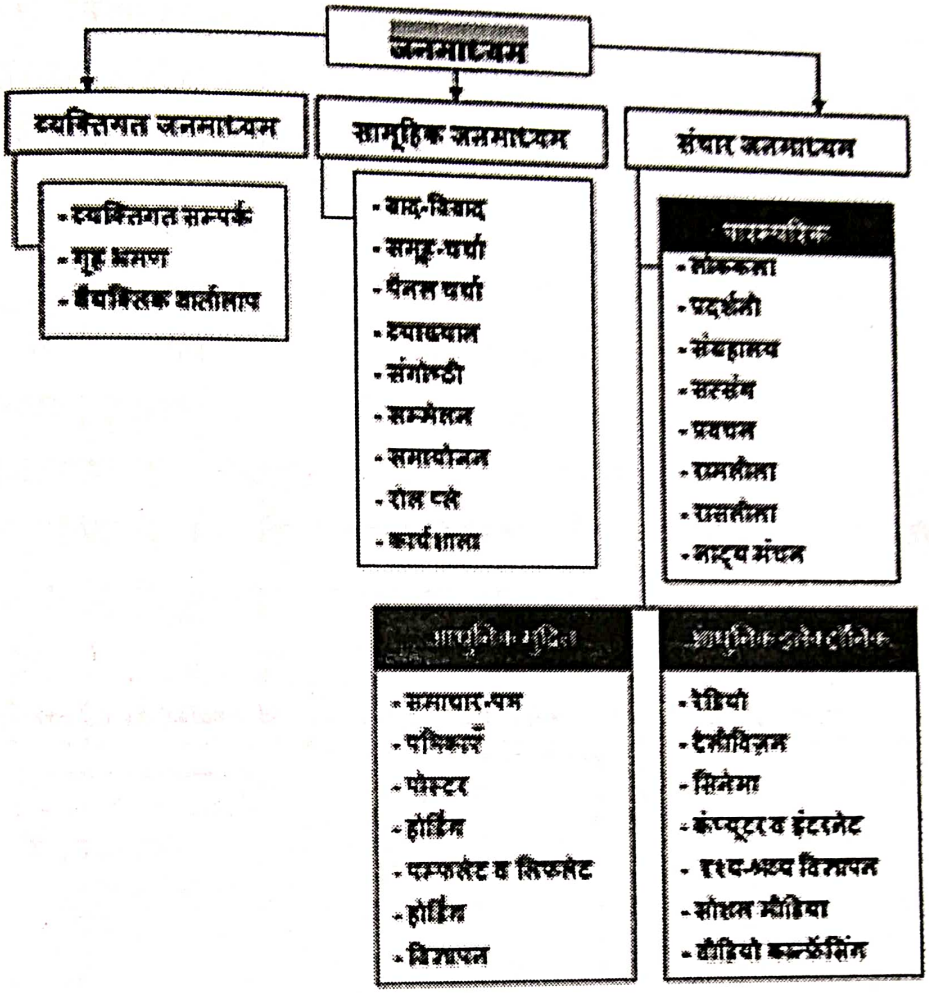
जनमाध्यम लेखनः परिचय, भूमिका एवं स्वरूप

डॉ० राजीव रंजन प्रसाद*

सामाजिक–प्राणी के रूप में मनुष्य बोलने–सुनने–समझने योग्य तो है ही वह लेखन–कला में भी पारंगत है। बोलने वाला प्राणी होना एक जन्मजात नैसर्गिक गुण है जिसके माध्यम से वह बाद में भाषा अर्जित करता है और तदुपरांत लिखना। वास्तव में बोलना और सुनना अभिव्यक्ति–कुशल व्यक्ति का सशक्त औजार है, किन्तु लिखना एक विशेष विधा है। यह प्रभावशाली माध्यम है जिसमें प्रयत्नपूर्वक जरूरी दक्षता व कुशलता हासिल की जाती है। माध्यम लेखन में यह रचाव–बनाव अधिक दिखलाई देता है। माध्यम लेखन का महत्त्व है, क्योंकि आज का युग सूचना युग है। माध्यम की विभिन्नता ने लेखन के स्वरूप, प्रकार, प्रस्तुति, प्रकृति, संरचना इत्यादि को काफी हद तक बदलकर रख दिया है। विभिन्न माध्यमों के द्वारा ज़ाहिर भाषा प्रायः मौखिक, लिखित, तकनीकी रूप में प्रकट की जाती हैं। ध्यान दिया जाना चाहिए कि जहाँ मौखिक भाषा में देहभाषा बेहद क्रियाशील होती है, वहीं लिखित भाशा में विचार–दृष्टि का सुगठित व सुव्यवस्थित होना उपयुक्त माना जाता है। जबकि तकनीकी भाषा में प्रयोजन–प्रयुक्ति आधारित अनुप्रयोग सर्वाधिक महत्त्वपूर्ण होते हैं। इलेक्ट्रॉनिक न्यू मीडिया का यह दौर 'डिजिटलाइजेशन युग' के नाम से जाना जा रहा है। मानवसुलभ आवश्यकताओं तथा पारम्परिक एवं आधुनिक जनमाध्यम के दायरे में बहुत सारी चीजें शामिल हैं जिनका महत्त्व उल्लेखनीय है।

सामाजिक प्राणी के रूप में व्यक्तिगत एवं सामूहिक जनमाध्यम के द्वारा असंख्य कार्यकलाप घटित होते हैं। उनके बीच में आपसी अंतःक्रिया सम्बन्धी आदान–प्रदान चलते रहते हैं; लेकिन प्रिंट एवं इलेक्ट्रानिक माध्यम

* सहायक प्रोफेसर, हिन्दी विभाग, राजीव गाँधी विश्वविद्यालय, रोनो हिल्स, दोईमुख, अरुणाचल प्रदेश–791112,



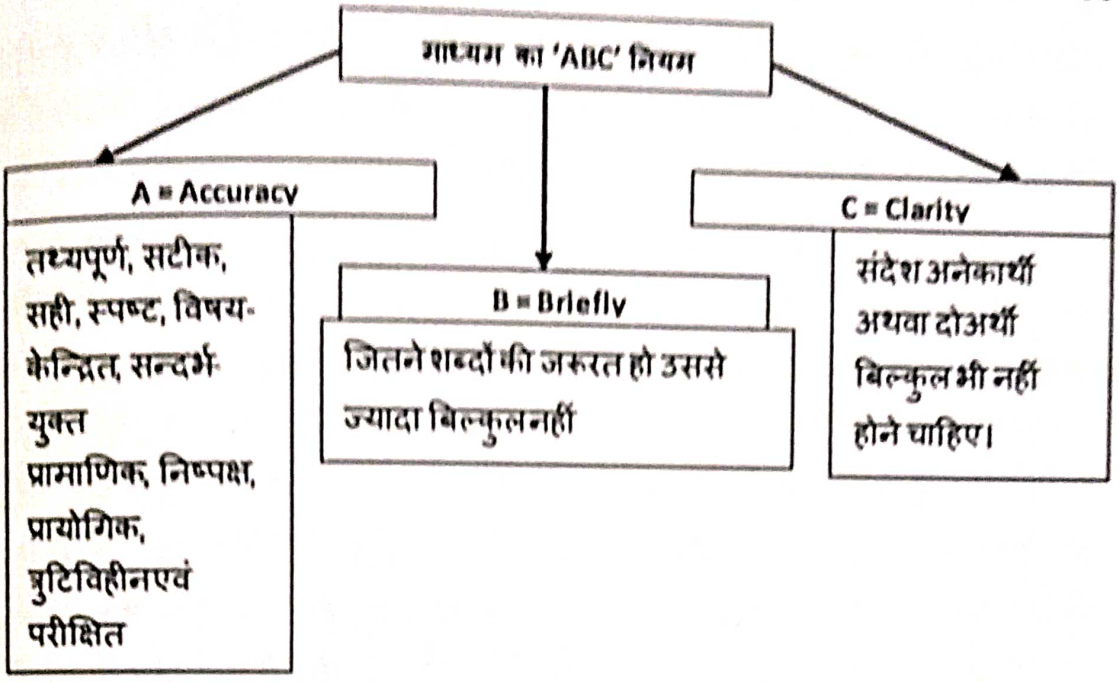
विशाल जनसमुदाय तथा व्यापक परिक्षेत्र के ऊपर अपना प्रभाव डालते हैं। इस तरह के आधुनिक माध्यम अंततः जनमत–निर्माण को ही अपना अनंतिम लक्ष्य मानते हैं। यह जनमत निर्माण कई सारे अनुशंगी उद्देष्यों की पूर्ति भी करते हैं। जैसे–मत निर्माण, विचार निर्माण, दृष्टि निर्माण, योजना निर्माण, कार्यक्रम निर्माण, नीति निर्माण इत्यादि। माध्यम लेखन एक चरण : प्रक्रिया है, जिसकी प्रकृति स्थायी होने की बजाय अत्यंत गतिशील, प्रभावी एवं निर्णायक हुआ करती हैं। माध्यम लेखन का मुख्य लक्ष्य होता है–'सूचना', 'शिक्षा' व 'मनोरंजन' का उपयुक्त ढंग और समुचित तरीके से फैलाव, अभिसरण अर्थात् 'कन्वर्जेंस'। सूचना एवं शिक्षा जनजागरूकता के मुख्य औजार है। इस कारण विभिन्न माध्यमों द्वारा इनको प्रमुखता से जगह दी जाती है। कारण कि सोचने–समझने की प्रणाली विकसित करने में इनका योगदान अहम है। मनोरंजन यहाँ खास अर्थों में व्यवहृत होता है। मनोरंजन का सम्बन्ध मन–बहलाव या 'टाइम–पास' हरगिज़ नहीं है।

भारतीय दृष्टि में मनोरंजन कहने का आशय उन उपक्रमों से है जो मन–मस्तिष्क को रंजित करें यानी मन में रस और आनन्द के भाव पैदा करने में सहायक बने। इसलिए मनोरंजन से सम्बन्धित विषयों में काफी वैविध्य होता है।

माध्यम परिचय और जनमाध्यम लेखन :

माध्यम एक सेतु है, संदेशों के आवागमन को निर्बाध तरीके से जारी रखने के लिए। इस प्रक्रिया में दो लोगों की भूमिका महत्त्वपूर्ण मानी जाती है; पहला वह जो कहने वाला है और दूसरा वह जो कही बात को सुनने की स्थिति में है। संचार की भाषा में कहने वाले को संचारक, सम्प्रेषक प्रेषक कहते हैं, तो सुनने वाले के लिए प्रापक, ग्रहणकर्ता शब्द प्रयोग में लाये जाते हैं। जबकि सामान्य शब्दावली में वक्ता व श्रोता कहना पर्याप्त है। माध्यम की दृष्टि से संदेश अत्यंत महत्त्वपूर्ण है; लेकिन संदेश पर कई बार माध्यम इतना वज़नी पड़ जाता है कि संदेश गौण हो जाता है और माध्यम की भूमिका प्रधान हो जाती है। संचार–विशेषज्ञ मार्शल मैकलुहान को माध्यम की ताकत पर इतना ज्यादा विश्वास था कि वे कहा करते थे– 'माध्यम ही संदेश है' यानी 'मीडियम इज दि मैसेज'। माध्यम–लेखन के जानकार मानते हैं कि माध्यम द्वारा व्यक्त विचार में सम्प्रेषक द्वारा कम से कम स्पष्टीकरण दिया जाना चाहिए, वहीं दूसरी तरफ श्रोता की ओर से वांछित प्रतिक्रिया अवश्य प्राप्त की जानी चाहिए। माध्यम की भूमिका में संदेश के महत्त्व को स्थापित करने के लिए संचार का (ABC) नियम बनाया गया है जिस बारे में आगे विवरण प्रस्तुत किया जाना आवश्यक है।

माध्यम मानवीय–क्रियाकलाप से जुड़ा हुआ है। मनुष्य के सारे क्रियाकलाप अथवा स्वैच्छिक गतिविधियाँ मनुष्य के सोच व चिंतन के ही नहीं, अपितु उसके द्वारा प्रयुक्त बहुविध माध्यमों के दायरे में भी आते हैं। दरअसल, भाषा मात्र सम्प्रेषण का साधन अथवा औजार मात्र नहीं है, वह अन्य लोगों के साथ सम्बन्ध बनाने और उनका निर्वाह करने का सशक्त माध्यम भी है। इसी प्रकार भाषा हमारे समाजीकरण एवं संस्कृतिकरण का माध्यम है। अतः वह एक अभिन्न व पूरक सत्ता के रूप में हमसे जुड़ा है; हमारे आदत–व्यवहार में विद्यमान है।



माध्यम लेखन की बात करें, तो भाषा एवं लिपि का महत्त्व अन्यतम है। भाषा को दीर्घायु बनाने में लिपि का योगदान सर्वोपरि है। कंप्यूटर के आगमन, दख़ल और बढ़ते प्रभाव ने लेखन के क्षेत्र में ताज्जुबकारी 'कंटेंट वेव' को जन्म दिया है। हिंदी का ही उदाहरण लें, तो यूनीकोड में सभी तरह के भाषिक–प्रतीक बनाए जा सकते हैं। यथाः अक्षर, शब्द, पद, पदबंध, वाक्य आदि। नानाविध गुणसम्पन्न कंप्यूटर की अपनी सीमाएँ भी हैं। पहला तो यही कि वह पूर्णतया मनुष्य पर निर्भर है। वह एक डिजिटल मशीन मात्र है जो हमें तमाम तरह की सुविधाएँ मुहैया कराता है। अतः लेखकीय–कौशल के लिए व्यक्ति ही मुख्य धुरी है। यद्यपि लिखना हर किसी के वश की बात नहीं है। दूसरे लिखना व्यक्ति–विशेष की इच्छा पर निर्भर है। सनद रहे, रचनात्मक एवं प्रभावी लिखने के लिए कठिन श्रम करना पड़ता है। बेहद अभ्यास से अपने लेखन को साधना होता है। सरल एवं सहज बोधगम्य भाषा में लिखना तो और कठिन तप है। अतएव, समाचार लेखन हो या रेडियो लेखन या कि सिनेमा हेतु पटकथा लेखन; सबकुछ हमारे इस दिशा में किए जा रहे कार्य एवं सोचने के ढंग पर निर्भर है। वास्तव में, लेखन सम्बन्धी बारीकियों को समझे बिना लेखन–कार्य में दक्ष–प्रवीण होना संभव नहीं है। कुछ भी लिखना अथवा कैसे भी लिख लेना वाला रवैया हमें परीक्षा में पास तो येन–केन–प्रकारेण करा सकते हैं, किन्तु ज्ञान एवं अनुभूति के लिए, संवेदना और दृष्टि के लिए, विचार एवं

प्रज्ञा हेतु यह तरीका बिल्कुल अपर्याप्त है। जिस तरह अच्छा वक्ता होने के लिए बेहतर श्रोता होना आवश्यक है; उसी तरह अच्छा लेखक बनने के लिए बेहतरीन और धैर्यशील पाठक/श्रोता/दर्शक बनना बेहद जरूरी है।

यदि हम जनमाध्यम–लेखन का इतिहास देखें, तो लिखे–छपे अक्षरों की वास्तविकता समझ में आ जाती है। यद्यपि उसका यहाँ विस्तार आवश्यक नहीं है, फिर भी हमारी दृष्टि में इनका स्मरण समीचीन है। यह सर्वमान्य तथ्य है कि लिपि ने लेखन को व्यापकता प्रदान की। लिपि द्वारा बोले जा रहे ध्वनि–प्रतीकों को यादृच्छिक भाषिक–प्रतीकों में ढाला गया जो शब्दार्थ के स्तर पर समान भाव–संवेदना एवं विचार–मूल्य वाले थे। प्राचीन काल में भारतीय विद्वजनों द्वारा अत्यधिक श्रम, अभ्यास एवं चिंतन द्वारा प्रभूत लेखन–कार्य हुआ जिन ग्रंथों, टीकाओं, भाष्यों, महाकाव्यों आदि का सांस्कृतिक–साहित्यिक महत्त्व आज भी सर्वाधिक है। प्रिंटिंग प्रेस के आविष्कार और आधुनिक मुद्रण–कला ने लेखन की दिशा में क्रांतिकारी बदलाव लाने का काम किया है। इसके द्वारा असीम उपलब्धियाँ और लोकप्रिय ख्याति पा लेने के बावजूद प्राचीन पांडुलिपियों/शिलालेखों आदि का महत्त्व कहीं किसी दृष्टि से कम नहीं हो जाता है। क्योंकि मुद्रण मषीन ने सबसे पहले धार्मिक ग्रंथों आदि का प्रकाशन–कार्य किया, ताकि जनसमाज में धर्म की वास्तविक प्रतिष्ठा संभव हो सके। भारत में मुद्रण–व्यवस्था एवं प्रकाशन होने के कारण आधुनिक प्रवृतियाँ भी आधुनिकता के वेष–बाने में आने लगी। इन में कुछ प्रमुख प्रवृत्तियाँ थीं–प्रश्नाकुलता, संशयशीलता, जीवन के आस्वादन में विश्वास, नए मूल्यों का अन्वेषण, तकनीकी आकर्षण, मोहयुक्त यथार्थवाद, समाजवादी वैचारिकी, मार्क्सवादी धारणा का सूत्रपात, जनतांत्रिक ढाँचे का निर्माण, मनोवैज्ञानिक व मनोविश्लेषणवादी अनुप्रयोग इत्यादि।

आधुनिक जनमाध्यम और समाचार पत्र–पत्रिकाएँ :

भारत में प्रेस के आगमन से अभूतपूर्व बदलाव हुए। सबसे पहला काम तो इस माध्यम ने यही किया कि जनसाधारण को तर्क करना सिखाया, शिक्षित होने की प्रेरणा दी और बराबरी पर आधारित जनतंत्र की माँग शुरू की। यद्यपि लोकभाषा में समाचार–पत्र का प्रचलन बहुत बाद का ईजाद है, तथापि इसने पराधीन भारतीयों को सपने देखने के लिए आँख दिए, तो

सोचने के लिए दिमाग़–बोध का परिष्कार कराया। 1800 ई. में फोर्ट विलियम कॉलेज की स्थापना भारतीय जनता के प्रगतिशील और आधुनिक होने का सच्चा प्रमाण बना। यह सब रुक-रुककर होता रहा। भारत समाज–सुधार के साथ राजनीतिक चेतना के निर्माण में जुटा था। इस प्रक्रिया में मुद्रित माध्यम के रूप में समाचार पत्र–पत्रिकाओं की भूमिका सर्वप्रमुख थी। इन सबसे स्थानीय–क्षेत्रीय जनभाषा का जो एक अखिल भारतीय स्वरूप बना हिंदी उनमें से एक है। उन्नीसवीं शताब्दी के आरंभिक दिनों में भारतीय भाषाओं में पहली बार बांग्ला का अवतरण हुआ और उसके ठीक बाद हिंदी का। दरअसल, आधुनिक लेखन–परम्परा में समाचार–पत्र उस सेतु के समान है जिसने लोक–संवाद हेतु भारतीय भाषाओं को संजीवनी प्रदान की।

सिनेमा, रेडियो और टेलीविज़न से पूर्व प्रचलित समाचार–पत्र एवं पत्रिकाओं की बात करें, तो इसकी विकास–यात्रा भी दिलचस्प है। अर्थात् मुद्रित माध्यम जिसे अंग्रेजी में 'प्रिंट मीडिया' कहा जाता है की तो बात और ठाट दोनों निराली है। हिंदी में समाचार–पत्र की छपाई उन्नीसवीं सदी में शुरू हुई। पहला हिन्दी साप्ताहिक अख़बार पंडित युगल किशोर शुक्ल के सम्पादन में कलकत्ता से सन् 30 मई, 1826 में प्रकाशित होना शुरू हुआ। इसके बाद तो हिंदीपट्टी मानों सोए से जाग उठा। नवजागरण का प्राक्कथन इन्हीं दिनों लिखा गया जिसमें राजा शिवप्रसाद सितारेहिंद, भारतेन्दु हरिश्चन्द्र, प्रताप नारायण मिश्र, बालमुकुन्द गुप्त, बालकृष्ण भट्ट इत्यादि भाषा के सच्चे साधक शामिल थे। देखते ही देखते गुलामी से बँधे–कसे भारतीयों में चेतना का संचार होने लगा। लिखने–पढ़ने की इस नई रवायत के कारण सबलोग आपस में संवाद करने लगे। वे समाचार–पत्र के रूप में एक शक्तिशाली औज़ार पा गए। भारतेन्दु जैसे पत्रकारिता के श्रेष्ठ उन्नायकों ने भारत–दुर्दशा के लिए यथास्थितिवाद और किंकर्तव्यविमूढ़ की प्रवृत्ति को जवाबदेह ठहराया। यह कहा जाने लगा कि अंग्रेज हमारे शोषण का कम बल्कि हमारे भीतर बैठे आपसी भेदभाव की भावना के कारण अपना हुक्म हम सब पर चला रहे हैं। आपसी झगड़े, रंजिश, शत्रुता के कारण पूरे देश में एकजुटता का अभाव है। बाहरी विचारधारा और मानसिकता वाले लोग हमारी भलाई क्यों चाहेंगे जब हम खुद ही

एक–दूसरे का अहित करने का सोचे बैठे हों। अंग्रेजी शिक्षा ने स्वतन्त्रता यानी गुलामी से मुक्ति को मनुष्य की बेहतरी का प्रतीकचिह्न बतलाया। इसके अतिरिक्त उनका बल समानता और बंधुत्व पर अधिक था। भारतीयों में यह भावना बलवती होने लगी कि स्वाधीनता से बढ़कर कोई चीज नहीं है। इस बारे में खूब लिखा–पढ़ा गया। यह दौर ही नवजागरण का कहलाया। अख़बार और पत्र–पत्रिकाओं ने कड़े प्रेस कानून होने के बावजूद अपनी राष्ट्रीयता के लिए वे सब दुःख–तकलीफ़ सहे, जिसकी कल्पना मात्र हमारी आत्मा को झकझोर देने वाला है। समाचार का काम हर राष्ट्र में चैथे खंभे का होता है। जन–संवेदना एवं जन–सरोकार की सबसे अधिक पूछ एवं उनकी रक्षा प्रेस करता आया है। आज प्रेस या समाचार–पत्र भले अपना महत्त्व खो चुके हों लेकिन एक समय था जिस समय अकबर इलाहाबादी का यह शेर बेहद मशहूर था–'खींचों न कमानो को और न तलवार निकालो, जब तोप मुकाबिल हो तो अख़बार निकालो।' वह घड़ी कुछ और था। समाचार–पत्रों के पास स्वतंत्र विचार–दृष्टि हुआ करती थी। वे निष्पक्षता एवं पारदर्शिता के मिसाल थे।

आज भी समाचार–पत्र टेलीविज़न से अधिक विश्वसनीय और आमजन के करीब हैं। उनमें लेखन सम्बन्धी वैचारिक गहराई और स्थानीय–वैश्विक परिप्रेक्ष्य का समुचित आकलन टेलीविज़न की तुलना में बेजोड़ है। इस समय आर्थिक तौर पर लघु पत्र–पत्रिकाओं की स्थिति दयनीय है जबकि बड़े पूँजी–सामर्थ्य वाले प्रकाशन–व्यवसाय आज भी अच्छी स्थिति में हैं। यह और बात है कि विचार एवं दृष्टिकोण की असल जान–प्राण अगर कहीं दिखलाई पड़ती है, तो उनमें लघु पत्र–पत्रिकाओं का नाम अग्रणी है। गुणी तथा विवेकवान सम्पादक अपना पत्रकारीय–धर्म नहीं भूले हैं। वे बाज़ार के असंगत दबाव के बावजूद अपना दायित्व–बोध अच्छे से निभाते हैं। उनकी दृष्टि में जनपक्षधरता का मूल्य सर्वोपरि है। इस नाते उनके चयन एवं प्रस्तुतिकरण अतिरंजता और सनसनीपन का शिकार नहीं हो पाते हैं। समाचार–पत्र का लेखन प्रायः सधा हुआ और विषय–सन्दर्भित होता है। सम्पादकीय–पृष्ठ वैचारिक आइने का सीधा गवाह होता है, इसलिए सम्पादक उसकी तैयारी अधिक सजगता एवं सावधानी के साथ करते हैं, ताकि जनसमाज को वास्तविकता बेलागलपेट

मालूम हो सके। इधर हाल के दिनों में समाचार–पत्रों ने अपनी गरिमा को अवश्य गिराया है, लेकिन इसकी आलोचना–समालोचना भी इसी बिरादरी ने सबसे अधिक की है। बात चाहे पेड न्यूज़ की हो या गोदी मीडिया की या फिर इम्बेडेड जर्नलिज़्म एवं समाचार–मिलावट की; समाचार–पत्रों ने इस तरह के सार्वजनिक चलन को पत्रकारिता के स्वास्थ्य के लिए सबसे हानिकारक माना है।

जनमाध्यम की भारतीय दृष्टि की बात करें, तो किसी भी पत्र–पत्रिका का सम्पादक रचनाकार और पाठक के बीच मध्यस्थ होता है। प्रकाशन–पूर्व पत्रिका के सम्पादन की जवाबदेही उसी की होती है। उसका प्रयास होता है कि सम्पादित रचनाएँ भ्रामक एवं त्रुटिपूर्ण न हो। इसके लिए कॉपी–सम्पादक का विषय सम्बन्धी विशेषज्ञता अनिवार्य है। यदि सम्पादित सामग्री साहित्य और कला विषयक हो, तो वह विशेष सतर्कता बरतता है। दुहराव और उलझाव से बचने की हरसंभव कोशिश करता है। सम्पादकीय अंतर्दृष्टि सम्पादन के अन्तर्गत उपयुक्त स्थान प्राप्त करती है। इसी कौशल के आधार पर वह परस्पर विरोधाभास व्यक्त करने वाले असंगत वाक्यांशों को अलग कर देता है, ताकि रचना का कोई भी अंश विरोधाभासी अथवा बेमेल नहीं लगे। सम्पादकीय–कार्य से जुड़े लोगों के भीतर कुछ खूबियों का होना आवश्यक है। यथाः विशेषज्ञता, इतिहास–बोध, अनुभव एवं अंतर्दृष्टि, कल्पनाशीलता, व्यापक दृष्टिकोण, सम्यक् विचारधारा और सचाई का आग्रह, कार्यशैली में एकरूपता, स्पष्ट वैचारिकी और भविष्य–योजना, परिवेश एवं देशकाल–बोध, तकनीकी सम्पादन–कौशल का ज्ञान, भाषा पर पकड़, चयनित पाठ का वस्तुपरक अन्तर्वस्तु विश्लेषण, सार्थक एवं प्रभावशाली प्रस्तुतिकरण का विवके, नूतन–नवीन प्रयोगों का समर्थक, कलात्मक चित्रों का उपयुक्त चुनाव, पूर्वाग्रह मुक्त, सम्पूर्णता की खोज, निर्णय की क्षमता, सामाजिक–सांस्कृतिक पक्ष और प्रभाव के प्रति सचेष्ट, पाठकीय मनोभाव और मनोगत संप्रत्ययों की समझ और पड़ताल, विश्व–मानव के निर्माण का लक्ष्य, सार्वदेशिक सांस्कृतिक आदान–प्रदान के लिए सुनियोजित प्रयास एवं प्रोत्साहन इत्यादि। जनहित और जन–सरोकार को प्राथमिकता देने वाले सम्पादकों ने अपने लिए सम्पादकीय मूल्य निर्धारिक कर रखा है। जैसे–तथ्यपरकता, वस्तुनिष्ठता, निष्पक्षता, संतुलन, स्त्रोत का उल्लेख

आदि। ऐसा नहीं है कि इन सब का अनुपालन करते हुए सम्पादक को किसी चुनौती अथवा संकट से जूझना न पड़ता हो; बल्कि वे बहुत सारे हैं। उदाहरणस्वरूप पूर्वग्रह, अतिरिक्त झुकाव, अवांछित दबाव, आवारा पूँजी से मुठभेड़, शासकीय या सरकारी–तंत्र द्वारा पिछलग्गू बनाए जाने का ख़तरा इत्यादि।

अतः समाचार–पत्र लेखन में एक पत्रकार ख़तरों के खिलाड़ी की भूमिका में होता है। वह सदैव दोधारी तलवार पर चलता है। मुद्रित माध्यम लेखन के रूप में समाचार पत्र–पत्रिकाओं का महत्त्व है, तो इस कारण भी कि यह बौद्धिक जागरण एवं जन–जागृति का सशक्त औजार है। जनता में स्वातंत्र्य–बोध और स्वाधीन आकांक्षा कायम रहे, इसको लेकर भी यह माध्यम सदैव सजग रहता है। इसके अतिरिक्त इस माध्यम में किए जाने वाले अधिसंख्य लेखन लोककल्याणकारी कार्य से सम्बन्धित तथा सुधारवादी दृष्टिकोण को सम्बोधित करने वाले होते हैं। इन्हीं विशेषताओं के कारण आज भी समाचार पत्र–पत्रिकाओं की ख्याति बहुत है। उन्हें जनमाज का दिशासूचक और जनशक्ति के रूप में उन्हें लोकतंत्र का चौथा खंभा अथवा चौथा स्तंभ कहा जाता है।

आधुनिक जनमाध्यम और रेडियो, सिनेमा, टेलीविज़न व कंप्यूटर :

रेडियो भारतीय जनता की सामूहिक आवाज़ बनी जिसका नाम रखा गया– 'ऑल इंडिया रेडियो'। आजादी के पश्चात आकाशवाणी ने वाचिक–शैली की नई स्वरलहरियों से सबको परिचित कराया। उन दिनों सिनेमा भारतीय सरजमीं पर अपना बसेरा बना चुकी थी, किन्तु वह फिलहाल गूँगी थी। रेडियो के आगमन के बाद सिनेमा भी बोलने लगी, वह 'टॉकी' हो गई। जल्द ही रेडियो और सिनेमा छा गए। दोनों जनमाध्यमों ने भारतीय ज़मीं में रची–बसी सामूहिक रागात्मकता एवं कल्पनाशक्ति को सजीव अर्थच्छटाओं द्वारा बिखेर दिया। इन बदलावों के दौरान लेखन प्रत्यक्ष–परोक्ष ढंग से शामिल रही। रेडियो का प्रभाव दूर–दराज के इलाकों में होता गया, क्योंकि उसकी शैली बातचीत की थी। एक तो बेहद अपनापन से भरी हुई, दूसरे मानवीय आवाज़ की मिठास से भरपूर। छोटे–छोटे वाक्यांश में कही–सुनी जाने वाली बातों में साधारणीकरण

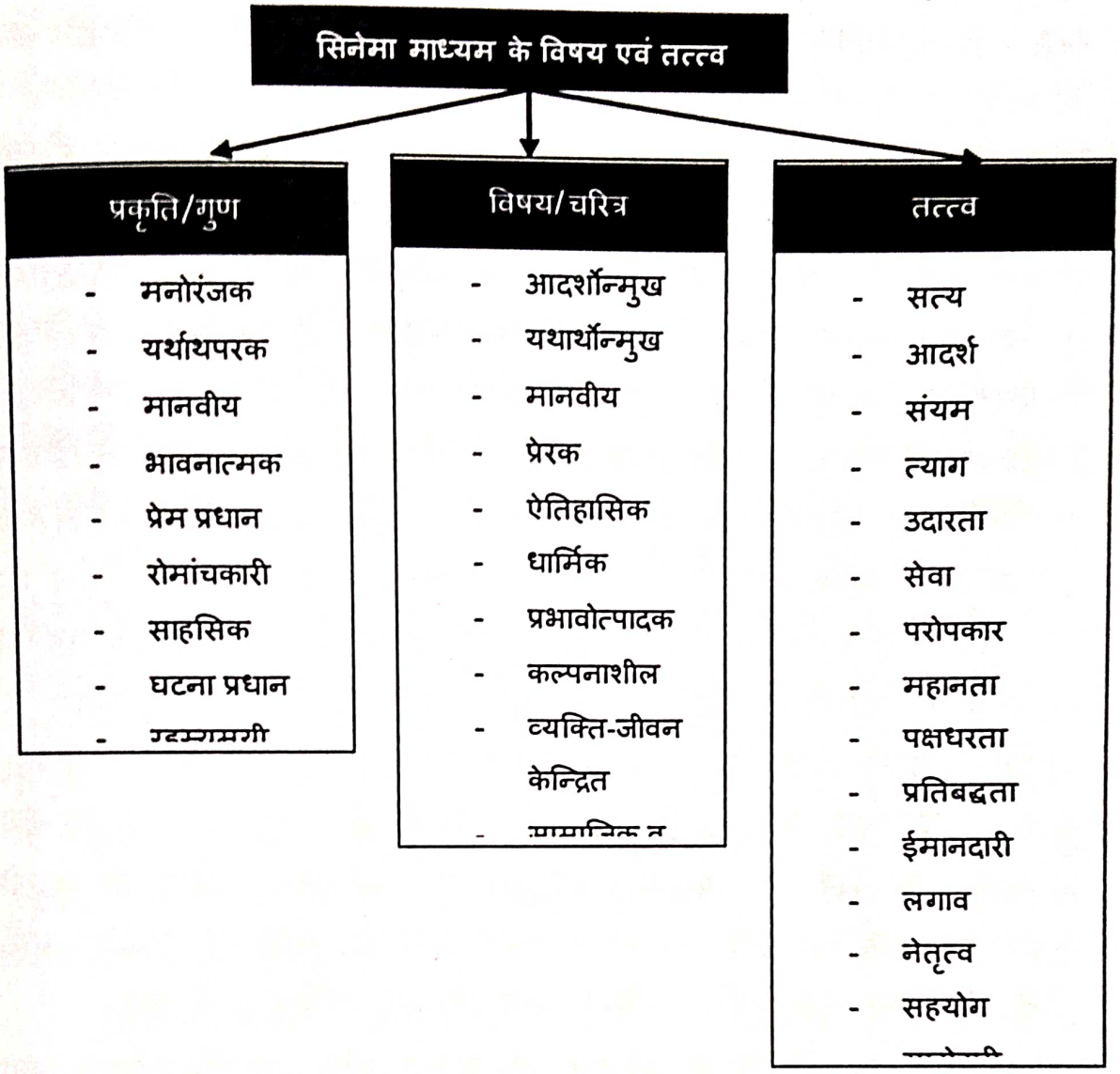
जबर्दस्त तरीके का था। वह गीत–संगीत के द्वारा लोगों का मनोरंजन कर पाने में सफल सिद्ध हो रही थी। इससे इतर सूचना एवं शिक्षा के पर्याय के रूप में भी आमजन से रेडियो का रिश्ता मजबूत हो रहा था। उसकी निकटता आवाज़ के बरास्ते पूरे देश–देशांतर से बढ़ने लगी थी। आज देश में रेडियो की पहुँच भारत के करीब 92 प्रतिशत आबादी–क्षेत्र तक है। आजादी के समय भारत में रेडियो स्टेशन की संख्य 9 थी जो बँटवारे के उपरांत भारतीय परिक्षेत्र के लिए छह ही बच गई; आज उनकी संख्या देशभर में 419 है। एक रिपोर्ट के मुताबिक रेडियो की लोकप्रियता आज भी चरम पर है। आज अकेले आकाशवाणी की ओर से 647 कार्यक्रम हर रोज प्रसारित किए जाते हैं। लगभग 90 भाषाओं में कुल 56 घंटे आकाशवाणी अपना निर्बाध प्रसारण करता है। यह बड़ी उपलब्धि है जिसका श्रेय रेडियो को जाता है।

इसी तरह रचनाशील लेखकों ने सिनेमा–पटकथा को नई धार दी। कई फ़िल्में ऐसी बनी जो मूलतया साहित्यिक कृतियों की भावभूमि (प्लॉट) पर आधारित थीं। जैसे–सुजाता, शतरंज के खिलाड़ी, सारा आकाश, आँधी, हजार चैरासिवें की माँ आदि। सिनेमा माध्यम ने तद्युगीन पीढ़ी को सांसारिकता से पिंड छुड़ाने की बजाए समकालीन परिस्थितियों से लड़ने–भिड़ने की चुनौती पेश की। गुरुदत्त, राजकपूर, देवानंद, दिलीप कुमार, सुनील दत्त जैसे अभिनेताओं की अदायगी और संजीदगी गौरतलब है। इसी दौर में अमिताभ बच्चन और धर्मेन्द्र के रूप में 'यंग्री यंगमैन' का जन्म हुआ। मिथुन चक्रवर्ती और अनिल कपूर भारतीय घरेलूपन का युवा चेहरा बनकर उभरे। आशिकी एवं इश्क़ के नवोदित चेहरे आमिर, सलमान, शाहरूख की तिकड़ी जबरदस्त रही। सुनील शेट्टी और अक्षय कुमार जहाँ स्टंट हीरो के रूप में लोकप्रिय हुए तो सनी देओल और अजय देवगन की 'ऑलराउंडर छवि' का सभी ने लोहा माना। अभिनेत्रियों में नरगिस, मधुबाला, मीना कुमारी, हेमा, जया, स्मिता, रेखा, शबाना, माधुरी, करिष्मा के नाम अव्वल हैं जिनका भारतीय दिलों पर अब भी राज है। यह समझना होगा कि सिनेमा मनोरंजन प्रदान करने का साधन है, लेकिन यही इसका एकमात्र लक्ष्य नहीं है। तभी तो अधिसंख्य फिल्मों में भारतीयता का ठेठ ठाट दिखाई देता है जिसमें अपने समय के दुख–संत्रास, तकलीफ़–पीड़ा

और विलाप का स्वर मुखरित था, तो नवचेतना से पूरित आधुनिक भारत का स्वप्न–संकल्प भी शनैः शनैः मूर्ताकार हो रहा था। आजादी बाद की उल्लेखनीय घटनाओं पर केन्द्रित कई सारी हिंदी फिल्में बनी जिसके केन्द्र में स्वाधीन भारत का बनता–बिगड़ता हुआ समाज था। नए तरीके के कलात्मक–रचनात्मक–बौद्धिक लोग इन माध्यमों से जुड़े। उन्होंने इन माध्यमों के लिए लिखा भी खूब। प्रेमचन्द जैसे अग्रणी साहित्यकार भी पीछे नहीं रहे। यह और बात है, बाद के दिनों में प्रेमचन्द ने फ़िल्म इंडस्ट्री से दूरी बना ली। कमलेश्वर, राजेन्द्र यादव, मनोहर श्याम जोशी जैसे प्रख्यात साहित्यकारों का फ़िल्मी अवदान उल्लेखनीय है। उदाहरण के रूप में अच्छी फ़िल्मों की लम्बी फ़ेहरिस्त सामने रखी जा सकती है जिसने भारतीय जनसमाज के बदलते चेहरे का हू–ब–हू चित्रण किया। प्रादेशिक भाषाओं ने भी कमाल के सिनेमाई ज़ज्बे का परिचय दिया। यथाः बाङ्ला, मराठी, तेलुगु, कन्नड इत्यादि।

सिनेमा के विषय व प्रकृति में मनोरंजन को प्राथमिकता प्रदान की गई है, तो इसका खास उद्देश्य है। दरअसल, नृत्य व गीत–संगीत को ही प्रायः मनोरंजन का का पर्याय समझ लिया जाता है जबकि यह पूरा सच नहीं है। अन्य माध्यमों की बात करें, तो मनोरंजन के साधन रूप में नाटक या प्रहसन का महत्त्व कमतर नहीं है। आज भी रेडियो कार्यक्रमों में 'हवा महल' बेहद लोकप्रिय प्रसारण है। इसी तरह हिन्दी धारावाहिकों में 'हम लोग' और 'बुनियाद' की लोकप्रियता कैसे भुलायी जा सकती है जिसने बाद के दिनों में रामायण एवं महाभारत जैसे पौराणिक धारावाहिकों को जन–जन तक पहुँचाने हेतु पूर्वमार्ग बनने का कार्य किया। इसी तरह सिनेमा का लोकवृत्त भारतीय जनजीवन के लिए मार्गदर्शक सरीखा साबित हुआ है। सिनेमा ने भारतीय जनसमाज को जिस कलात्मकता और खूबी के साथ सिने–परदे पर चित्रित किया, वह बेमिसाल है। आज भी सिनेमा को 'लार्जर दैन लाइफ' की दृष्टि से सबसे ऊपर रखा जाता है।

दृश्य–श्रव्य माध्यम का अगला जीवंत रूपाकार था–टेलीविज़न। भारत में टेलीविज़न प्रसारण पहली बार 15 सितम्बर, 1959 ई. से शुरू हुआ। उन दिनों टेलीविज़न की दुनिया आज की तरह कुहरीली नहीं थी। वही सबकुछ प्रसारित होता था जो समाज में रोज–ब–रोज घटित हो रहा



था। सत्य की इस पक्षधरता का ध्येय वाक्य था–'सत्यम् शिवम् सुन्दरम्'। यानी समाचार–पत्र, सिनेमा, रेडियो और आजादी के तुरंत बाद टेलीविज़न ने पूरा परिदृश्य ही बदल कर रख दिया। 1982 ई. में रंगीन टीवी के आगमन का व्यापक असर हुआ। टेलीविज़न का 'क्रेज' शुरू हुआ, तो आने वाले समय में श्वेत–श्याम के साथ रंगीन टीवी भी आम–चलन में शुमार हो गया। सांस्कृतिक दृष्टिकोण से देखें, तो भारतीयता की मूल–भावना और पारिवारिक–संस्कार को रचने–बुनने में टेलीविज़न को श्रेय देना सबसे उपयुक्त होगा। बीसवीं सदी के आख़िरी दशक आते–आते टेलीविज़न घर–घर में मनोरंजन का स्थायी विकल्प बन गया। इसने न केवल अपनी जगह बना ली, अपितु कई महत्त्वपूर्ण सामाजिक बदलाव भी किए। 'हम लोग' और बुनियाद' धारावाहिक ने भारतीय समाज का घरेलू चेहरा सामने

रखा, तो 'रामायण' एवं 'महाभारत' जैसे धारावाहिकों ने ऐतिहासिक मिथकों एवं पौराणिक गाथाओं को नई ऊँचाई प्रदान की। टेलीविजनों में समाचारों के महाएपिसोड (24×7) का दौर बहुत बाद में शुरू हुआ। बीसवीं सदी के एकदम आख़िर में। टेलविज़न पर न्यूज़ दिखाने–सुनाने की योजना बनायी–सुरेन्द्र प्रताप सिंह ने जिनके बाद की पीढ़ियों ने इसकी गरिमा को बनाए रखने में कोई कोर–कसर नहीं छोड़ा। टेलीविज़न मीडिया के प्रभाष जोशी कहे जाने वाले एस. पी. सिंह ने टेलीविज़न समाचारों के आवश्यक मानदण्ड तय किए और इसे लोकप्रियता के शिखर तक पहुँचाया। आज परिदृश्य बदल चुका है। दृश्य–श्रव्य रूप का सशक्त माध्यम टेलीविज़न इन दिनों मुगल–मीडिया के कब्ज़े में है और इस पर हद दरज़े तक धंधेवाज होने का असहनीय दवाव है। तब भी एक माध्यम के रूप् में टेलीविज़न की भूमिका और महत्त्व आज भी अतुलनीय है; क्योंकि उसकी पहुँच और प्रभाव अन्य माध्यमों की तुलना में अधिक रोचक, मजेदार और समझने योग्य है। पहले तो 'रेडियो' और 'दूरदर्शन' विश्वसनीय जानकारी के पुख़्ता औज़ार थे। अख़वार कुछ जानने–समझने की पहली खुराक थी। इक्कीसवीं सदी का पहला दशक ख़त्म होते–होते ही समाचार–पत्रों और ख़वरिया–चैनलों के ई–पेपर/वेव ठिकाने चर्चित होने लगे।

अव समय 'डिजिटलाइजेशन' की वढ़ती माँग पर टिका हुआ था। अव सवकुछ कंप्यूटरीकृत भाषा में दर्ज थे। इन्हीं दिनों डिजिटल लाइब्रेरी के चलन ने हमें ज्ञान के अथाह स्रोत तक पहुँचा दिया जिसमें अपनी अभिरुचि एवं आवश्यकता के अनुरूप कोई भी मुद्रित/श्रव्य/दृश्य–श्रव्य सामग्री 'अक्सेस' यानी प्राप्त कर सकता था। अव इस उपलब्धता के कारण ऐतिहासिक महत्त्व के पांडुलिपियों एवं हस्तलिखित सामग्रियों का दस्तावेजीकरण किया जा सकना संभव हो गया है। हिंदी में ही आज सैकड़ों 'आर्काइव' हैं जहाँ ज्ञान–स्रोत का पिटारा या भण्डार सुरक्षित है। यही नहीं कई लुप्तप्राय ऐसी भाषाएँ जिनका अस्तित्व ही खतरे में पड़ा मालूम दे रहा था; के संरक्षण–संवर्द्धन हेतु 'डिजिटल आर्काइव' वनाए जाने लगे हैं। और यह सवकुछ माध्यम–लेखन की प्रक्रिया में कंप्यूटर के उपयोग व इंटरनेट की सुलभता के कारण ही संभव हो सका है।

जनमाध्यम लेखन का प्रक्रियागत स्वरूप व संरचना :

अक्सर यह कहा जाता है कि लिखी जाने वाली भाषा साफ, स्पष्ट, सहज, सुबोध, पठनीय, मर्यादित व आदरयुक्त होने चाहिए। पर प्रश्न उठता है, इतनी सारी अपेक्षाओं से पूर्ण लेखन हो तो कैसे हो। एक तो माध्यम की विविधता और दूसरे हर माध्यम में प्रयुक्त होने वाली बहुत सारी विधाएँ, माध्यम लेखन की कठिनाई को बढ़ाती ही नहीं चुनौतीपूर्ण बना देती हैं। सिर्फ रेडियो माध्यम की बाते करें, तो अनेकानेक विधाएँ प्रचलन में हैं। जैसे–समाचार, वार्ता, साक्षात्कार, परिचर्चा, नाटक, धारावाहिक, फीचर इत्यादि। मुश्किल तो यह कि विधागत रूप एवं शैलियाँ भी एकसमान नहीं है। कहीं किसी विधा में यह माँग होती है कि प्रस्तुत भाषा बेहद औपचारिक एवं बिल्कुल अभिधात्मक हो या कि उनमें अधिक से अधिक सूचनाओं की प्रधानता हो; तो दूसरी तरफ यह भी अपेक्षा रखी जाती है कि भाषा बेहद लालित्यपूर्ण, रोचक और अपने कहनकला में लाजवाब होने चाहिए; ताकि पाठक/श्रोता/दर्शक का वह बाँधे रखे, उनके दिलोंदिमाग पर उपयुक्त प्रभाव छोड़ने में सफल हो। ऐसी अवस्था में भाषा की मुहावरेदानी का बदल जाना स्वाभाविक है; शैली में लक्षणा व व्यंजना का समावेश किया जाना सर्वोचित है।

अतः जनमाध्यम–लेखन का कार्य आसान बिल्कुल नहीं है। कारण कि दिमाग में उपजे किसी विचार को हम यकायक भाषा में नहीं ढाल लेते हैं। दिलोंदिमाग में इसकी पूरी प्रक्रिया चलती है। बोले जाने से पूर्व जो मानसिक–शारीरिक प्रक्रिया दिमाग में घटित होती है उसे सचेतन अवस्था कहा जाता है। यानी बोलते वक्त हमें ज्ञात होता है कि हम जो बात कह रहे हैं वह कहाँ कह रहे हैं और क्यों व कैसे कह रहे हैं। सचेतन अवस्था में घटित इस मानसिक क्रियाकलाप को हम मनोभाषिकी कहते हैं। मनोभाषिकी असल में मन के स्तर पर बोली जाने वाली वह भाषा है जिसका अहसास तो होता है किन्तु उसमें आवाज़ अनुपस्थित रहती है; जिस कारण अर्थ का सम्प्रेषण संभव नहीं है। यानी मन ही मन किसी की प्रशंसा कीजिए, उसकी कोई मानसिक–छवि गढ़िए, उस पर आँखे टिकाए होने के बावजूद उसके कहे को नापसंद कीजिए; यह सबकुछ घटित अपने भीतर होता है लेकिन इस अनकहे की भाषा व्यक्त नहीं हो पाती है। इसे

मनोविज्ञान की भाषा में 'इन्टरनल स्पीच' या 'सेल्फ इमेजिनेशन' कहते हैं। अभ्यस्त होने के कारण मनुष्य इन रवैए का इस कदर आदी हो जाता है, मानो ये सबकुछ अपनेआप घटित हो रहे हैं, जबकि ऐसा बिल्कुल नहीं है। जिस तरह पढ़ने का इरादा न हो तो हम कतई पढ़ नहीं सकते हैं; उसी तरह लिखना भी प्रयत्नपूर्वक ही संभव है। इसकी पूर्व तैयारी अत्यावश्यक है। इसकी प्रक्रिया को अंजाम तक पहुँचाना पड़ता है। आपने किसी को 'टेक्सट मैसेज' भेजने को सोचा। क्या सोचने मात्र से वांछित संदेश अपने गंतव्य तक पहुँच जाएगा। नहीं न! उसके लिए संदेश लिखने होंगे या कंप्यूटर द्वारा टाइप करना होगा। अब तो कंप्यूटर के आने से लिखने और भेजने का झंझट नहीं रहा। अब हम बिना डाकघर गए, लिफाफ़े को चिपकाए बगैर अपना लिखा जिस किसी को त्वरित ढंग से भेज सकते हैं। अपना मोबाइल फोन तो सबसे स्मार्ट है। उसमें वर्ड डॉक्यूमेंट, पीडीएफ, पीपीटी सबकुछ खुल जाते हैं। सेल्फ़ी, वीडियो रिकार्डिंग, वायॅस चैट, वीडियो कॉलिंग इत्यादि तो आम बात है। लेखन–सामग्री हेतु अब धूल–धकड़ से सने किताबों पर हाथ फेरने की आवश्यकता नहीं रही। क्योंकि कई सारे ऐप और सॉफ्टवेयर स्मार्ट फोन में विराजमान हैं जिनके माध्यम से हम मनोवांछित सामग्री कंप्यूटर पर पढ़ सकते हैं। 'किंडल' एक ऐसी ही सुविधा का नाम है।

इन दिनों कंप्यूटर ने इंटरनेट के साथ मिलकर विशाल जालनुमा एक ऐसा आभासी जगह (वर्चुअल स्पेस) बना लिया है जिसमें दुनिया–ज़हान की सैर 'फ्रैक्शन ऑफ सेकण्ड' में संभव है। इस अन्तर्जाल को आजकल 'वर्चुअल वर्ल्ड' कहा जा रहा है तथा ये सब क्रियाकलाप जहाँ घटित होते हैं वे 'वर्चुअल स्पेस' कहलाते हैं। यह माध्यम पुराने सभी माध्यमों से दिलचस्प है क्योंकि यह मल्टीमीडिया यानी बहुमाध्यम है। मल्टीमीडिया का कमाल यह है कि एक ही जगह अब समाधान संभव है जो पहले अलग–अलग औजारों से हल किया करते थे। दरअसल, कंप्यूटर आधारित प्रोग्राम अथवा एप्लिकेशन उपलब्ध होने के कारण रेडियो, टेलीविज़न, सिनेमा, समाचार–पत्र, पत्रिकाएँ सबकुछ एकमेक हो गए हैं। अर्थात् लिखना, पढ़ना, सुनना, देखना, सुधार करना, तस्वीर बनाना, हटाना, जोड़ना, खोजना इत्यादि बहुविध कार्य कंप्यूटर एवं इंटरनेट द्वारा आसानी

से संभव है। अब हम बोलते जाएँ और हमारा मोबाइल उसका लिप्यांकन भी करता जाएगा। कंप्यूटर टाइपिंग और मनमाफ़िक टाइप–फेस चुनना वह सचाई है जिससे भाषा में छपी इबारतें बेहद मोहक एवं आकर्षक बन पड़ी हैं। खुद हिंदी के विस्तार–फैलाव में 'यूनिकोड' का महत्त्व अप्रतिम है। दरअसल, कंप्यूटर गुणों का खान है। जैसे–लेआउट, डिजाइन, ग्राफिक्स, एनिमेशन, कलर–कंट्रास्ट, साउंड इफेक्ट, पिक्चर एडिटिंग, वीडियो सर्फिंग, शेयर, अपडेट, मॉडरेट इत्यादि। रोजमर्रा की ज़िंदगी में कंप्यूटर के उपर्युक्त कामों का इस्तेमाल बढ़–चढ़ कर हो रहा है। क्योंकि आमजन से जुड़े इन लेखन–कार्यों को जनमाध्यम–लेखन कहा जा रहा है। विशाल भू–भाग में बसे लोगों तक अब सिर्फ संचार के पुराने 'एप्रोच' द्वारा पहुँच सकना संभव नहीं है। यथाः अन्तरर्वैयक्तिक संचार, समूह संचार, बातचीत, वार्ता, भाषण, घटना–विशेष के बारे में बहस–मुबाहिसे आदि।

अतएव, बीती सदी में समाचार–पत्र, रेडियो और टेलीविज़न के आगमन से 'सूचना–विस्फोट' का प्रादुर्भाव हुआ है जिसकी गिरफ़्त में आज पूरी दुनिया है। इस इक्कीसवीं सदी में कंप्यूटर और इंटरनेट ने तो 'सूचना', 'शिक्षा' एवं 'मनोरंजन' के क्षेत्र में 'आइस युग' का सूत्रपात कर डाला है। यह 'आइस युग' सूचना एवं संचार–प्रौद्योगिकी आधारित है जिसमें किताबों की पूछ घटी है, लेकिन तकनीकी–प्रौद्योगिकी आधारित 'डिजिटल पब्लिशंग' का दायरा अप्रत्याशित ढंग से बढ़ा है। सिनेमा और टेलीविजन इलेक्ट्रॉनिक मीडिया के सशक्त उदाहरण है। कंप्यूटर इससे चार कदम आगे हैं क्योंकि उसके द्वारा कई और काम भी निपटाए जा सकते हैं। कंप्यूटर अब एक प्राथमिक कौशल विकास का रूप ले चुका है। कंप्यूटर लिटरेसी पर बल ज्यादा है। इसी प्रकार इंटरनेट की विशेषताएँ बहुत सारी हैं। जैसे, इंटरनेट से जुड़े कंप्यूटर द्वारा मनपसंद गाने केवल सुन ही नहीं सकते हैं बल्कि उसे बाद के लिए सुरक्षित भी रख सकते हैं। इसको कहते हैं– 'डाउनलोड एण्ड सेव'। ये गाने जरूरी नहीं कि केवल सुनने वाले हों बल्कि वे आसानी से देखे–सुने और बाद में संग्रहित किए जा सकते हैं। विडियो की दृष्टि से यू–ट्यूब बड़ा ज़खीरा है। अब तो वीडियो के माध्यम से वीडियो–कॉन्फ्रेंसिंग होने लगे हैं। अक्सर टेलीविज़न

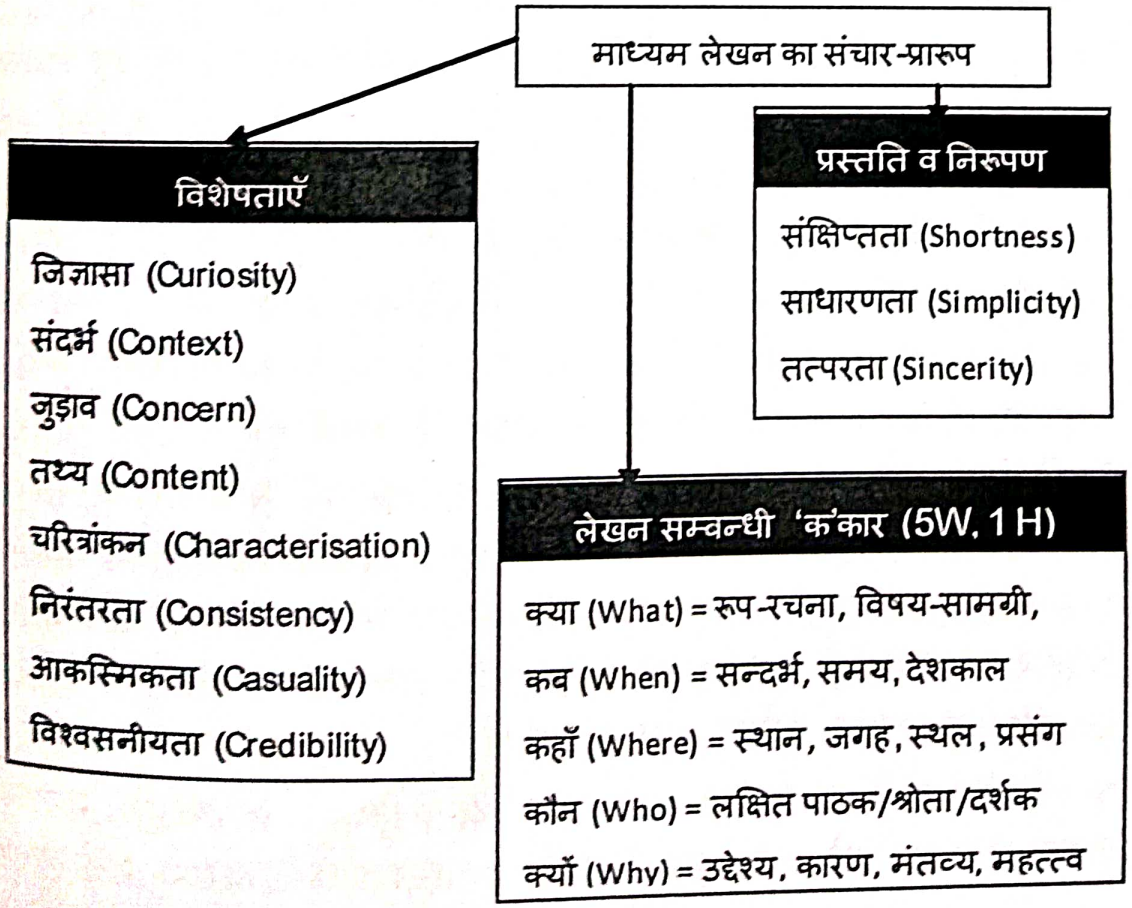
चैनलों में दूर बैठा व्यक्ति न्यूज़ रूम में बैठे व्यक्ति से 'लाइव' बातचीत कर लेता है।

समय के बदलाव के साथ सायास–अनायास ढेरों बदलाव होते चले जाते हैं। जैसे कुछ समय पूर्व तक रेडियो की लोकप्रियता बहुत अधिक थी। उसे आकाशवाणी के रूप में जाना गया। बाद मे विविध भारती (03 अक्तूबर, 1957 ई.) ने रेडियो कार्यक्रम में चार चाँद लगाए। आरंभ में सामुदायिक रेडियो ने इस अवधारणा को मजबूती प्रदान की कि 'रेडियो तरंगें सार्वजनिक संपत्ति है' जिस कारण व्यक्तिगत एवं सामूहिक प्रयासों द्वारा रेडियो प्रसारण की सामुदायिक सेवा शुरू हुई। उसके बाद रेडियो एफ.एम. का नया ज़माना आया जिसमें रेडियो जॉकी की अदा और शोखी ने सुनने वालों का मन मोह लिया। अब का हाल यह है कि रेडियो वेब–पोर्टल के माध्यम से भी बजने शुरू हो गए हैं। रेडियो द्वारा प्रसारित सामग्री विशेषकर समाचार अब ई–कंटेट के रूप में उपलब्ध हैं। शुरूआत में रेडियो पर कई मोहक शास्त्रीय और सुगम संगीत बजते थे। जरूरी एवं चर्चित विषयों पर परिचर्चा होती थी, तो कई बार गंभीर मुद्दों को लेकर विषय–विशेषज्ञ वार्ता प्रसारित करते थे। आज भी महात्मा गाँधी और सुभाष चन्द्र बोस के प्रसारण की खूब चर्चा होती है। रेडियो पर प्रसारित होने वाले नाटकों, प्रहसनों, झलकियों आदि की अपनी विशेष लोकप्रियता है। आजादी उपरांत भारत में बहुचर्चित रेडियो की घोषणा थी–'बहुजन हिताय, बहुजन सुखाय'। लोग सुन–सुना रहे थे–देशहित में, लोगों को जागरूक कर रहे थे–राष्ट्रहित में। उनकी मनोकामना में मंगल का उदय और संभावना के शुभ–चिह्न शामिल थे। राजनीति में हर तरह के लोग थे–किन्तु सबका मुख्य स्वर राष्ट्रीय चेतना से ओत–प्रोत था। निश्चित तौर पर साम्प्रदायिकता और असहिष्णुता हालिया ईजाद हैं जिन्हें जनसमाज के ऊपर एक राजनीतिक प्रोपेगेण्डा के तहत थोपा जा रहा है। यह मीडिया के जन–साख (मास–क्रेडिट) पर बदनुमा दाग है जिससे भारतीय जन और उनकी अंतरात्मा दोनों आहत है। मीडिया चाहे वह क्लासिकल हो या न्यू मीडिया अपने निज–स्वरूप में वह विश्वसनियता का पर्याय है। वस्तुनिष्ठता जनमाध्यम की एकमात्र कसौटी है। आज आवारा पूँजी के जोर–दाव ने वर्तमान परिदृश्य में भारी उलटफेर कर रखा है। नतीजतन

पत्रकारीय–निष्ठा में स्वार्थपूर्ण महत्त्वाकांक्षा इस कदर घुल–मिल चुके हैं कि पारदर्शिता का सदानीरा जल पीला होते–होते काला पड़ चुका है। इसे इन दिनों कई नामों से जाना जाता है। यथाः पेज थ्री, पेड न्यूज़, येलो जर्नलिज़्म, ग्रे प्रेस, इम्बेडेड, सरोगेट इत्यादि। इन अवांछित प्रभावों से माध्यम–लेखन और उसकी भाषा बुरी तरह क्षतिग्रस्त हुए हैं।

जनमाध्यमों की भाषा एवं लेखन–प्रविधि :

हर माध्यम की अपनी विशेषता होती है। उनकी अपनी सीमाएँ भी हैं। इस कारण हर माध्यम अपने को जनमाध्यम के रूप में प्रस्तुत करते समय अत्यंत सजग और सचेत होते हैं। माध्यम–लेखन की सामग्री भी माध्यम की अपनी मूल प्रकृति के अनुरूप ही तैयार की जाती हैं जिससे पाठक/श्रोता/दर्शक का जुड़ाव सीधा और स्वाभाविक हो। इसलिए माध्यम लेखन में एक खास तरह की एकरूपता, सम्बद्धता व स्वीकार्यता दिखलाई देती है। हर माध्यम का लक्ष्य अपने लक्षित पाठक/श्रोता/दर्शक तक सीधे पहुँचने एवं उन पर अपना प्रभाव छोड़ने की होती है। अर्थात् उनका लक्ष्य है–आम–आदमी, सार्वजनिक लोग, लोकजन, साधारण

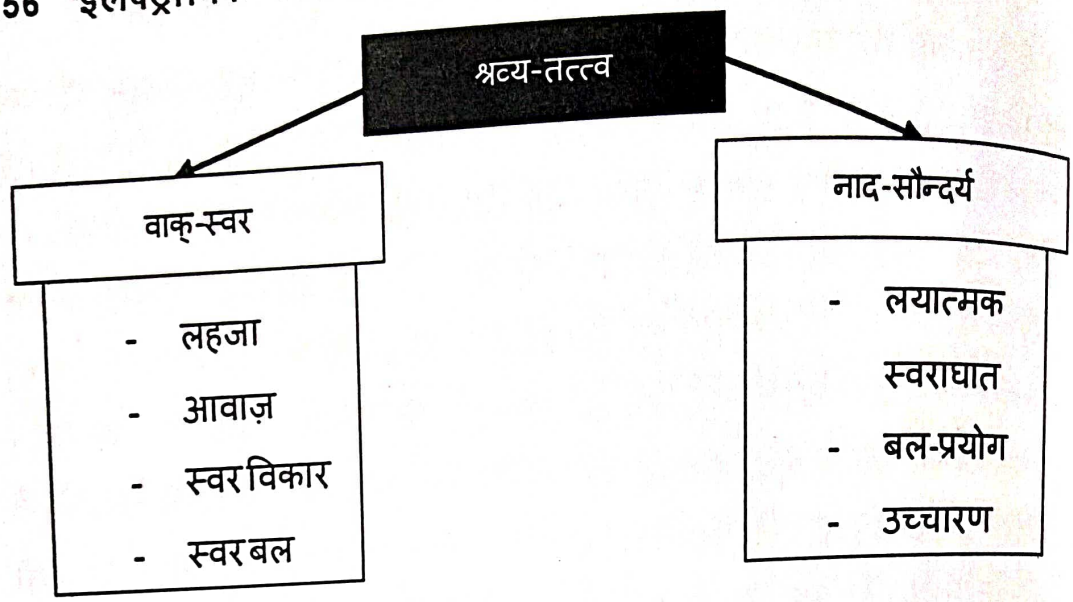


व्यक्ति इत्यादि। इसलिए माध्यम लेखक अपने द्वारा प्रस्तुत किए जाने वाले सामग्री की उपयुक्तता एवं उसकी वस्तुनिष्ठता पर बार–बार विचार करता है। वैज्ञानिक व तार्किक दृष्टि से वह उनके प्रसंग–संदर्भ व स्थान को सुनिश्चित करता है। सामान्यतः माध्यम लेखन की सामग्री तैयार करते समय माध्यम–लेखक कई सारे बिन्दुओं पर अपना ध्यान केन्द्रित करता है जिसे हम एक संचार–प्रारूप (मॉडल) द्वारा दिखा अथवा दर्शा सकते हैं।

मुद्रित माध्यम–लेखन की बात करें, तो समाचार–पत्र व पत्रिकाओं का ध्यान सबसे पहले आता है। समाचार पत्र–पत्रिकाओं के लिए लेखन मूलतः लेखकीय योग्यता की सघन परीक्षा है। यह सामान्यतया व्यावहारिक अनुभव, स्मृति, पूर्वज्ञान एवं प्रत्यक्षीकरण से सम्बन्धित होता है। समाचार पत्र–पत्रिकाओं की भाषा लिखित स्वरूप में होने के कारण बेहद सुगठित और निर्णायक होती हैं। उन्हें कुछ इस तरह शब्द, पद, वाक्य आदि में साधा जाता है कि उनके कहे का असर प्रभावशाली तरीके से पड़ता है। अतः मुद्रित माध्यम की लिखित भाषा में जिन तत्त्वों का समावेश होता है; वे हैं– (1) वस्तुनिष्ठ कथन, (2) शब्द संतुलन, (3) अर्थ–संकोच यानी संक्षिप्तता और (4) शुद्ध संरचना। माध्यम विशेषज्ञों की राय में लिखित माध्यम विशेषकर मुद्रित माध्यम हेतु लेखन–कार्य करते हुए यह ध्यान रखा जाना जरूरी है कि जो कुछ भी लिखा जाए वह अपने पाठकों को लक्ष्य कर अर्थात् उन्हें ध्यान में रखकर लिखना चाहिए। माध्यम–लेखक को अपने स्तर के साथ–साथ पाठकों के स्तर का भी पूरा ध्यान रखना चाहिए। समाचार पत्र–पत्रिकाओं की विषयवस्तु प्रायः तीन चीजों से सम्बन्धित होती हैं–सूचना, शिक्षा एवं मनोरंजन। माध्यम लेखनकर्ता को पत्रकारिता के इस मूल प्रकार्य को ध्यान में रखते हुए समस्त सामग्री लिखनी चाहिए। माध्यम लेखन को प्रवृत्त लेखक को कुछ विशिष्ट तत्त्वों (सकारात्मक एवं नकारात्मक दोनों) का स्मरण रखना चाहिए जो माध्यम लेखन की दृष्टि से महत्त्वपूर्ण है। जैसे–तथ्य संग्रहण, विचार, दृष्टिकोण, विश्लेषण, टिप्पणी, जनमत, लेखन पद्धति, तकनीकी अनुप्रयोग, घटना, समस्या, पूर्वधारणा, पूर्वग्रह, दुराग्रह इत्यादि।

यदि श्रव्य एवं दृश्य–श्रव्य माध्यम लेखन की बात करें, तो माध्यम लेखन में बोले जाने वाले शब्द ही नहीं महत्त्वपूर्ण होते हैं, उसके द्वारा व्यक्त

निरर्थक ध्वनियाँ भी काम की होती है। जैसे रेडियो व टेलीविज़न माध्यम में किसी वक्ता के लिए आवश्यक है कि वह बोलते समय हड़बड़ी बिल्कुल न दिखाए। सामान्य ढंग से साँस ले। साफ एवं स्पष्ट तरीके से बोलने के लिए मुँह, तालु और जबड़े से काम लेना पड़ता है, इसलिए इनका ध्यान रखना आवश्यक है। वाचन के दौरान मौनरूपी अंतराल विशेषकर रेडियो माध्यम में बेहद अर्थपूर्ण होती हैं। बोलने के दौरान विषय प्रवाह और लयात्मकता श्रोता एवं दर्शकों के दिलोंदिमाग पर अनूठा छाप छोड़ने में समर्थ होती हैं। सबसे पहले तो हमें लयात्मकता अथवा प्रवाह कहने का अभिप्राय क्या है, यह समझना जरूरी है। असल में, भावनाओं और विचारों के अनुरूप बोलने की शैली में परिवर्तन होते रहने को ही हम लयात्मकता कहते हैं। श्रव्य–माध्यम की तो यह केन्द्रीय अन्तर्वस्तु है, यानी प्राणतत्त्व। लयात्मकता के लिए अनुभवी विशेषज्ञों ने कुछ चीजें निर्धारित की हुई है। जैसे–मुख्य शब्दों पर विशेष बल/जोर देना, आवाज़ की ऊँचाई में परिवर्तन, बोलने की गति में परिवर्तन, मुख्य विचारों को पहले और बाद में रूकना इत्यादि। इसी तरह रेडियो पर कोई गंभीर बात प्रसारित की जानी हो, तो उसके लेखन के प्रति सजगता आवश्यक है। माध्यम लेखन करने वाले को तीन चीजों के समावेश पर ध्यान देना चाहिए–1) संक्षिप्तता, 2) रोचकता और 3) नवीनता। रेडियो की खूबसूरती उसके लेखकीय योग्यता से अधिक प्रस्तुत सामग्री की कलात्मकता में अन्तर्निहित होती है। सबसे दिलचस्प बात यह है कि रेडियो की सरलता को ही उसकी कलात्मकता माना गया है। यह अपेक्षा की जाती है कि रेडियो की शब्दावली सधी हुई हो, किन्तु उसमें इस्तेमाल शब्द आम प्रचलन व चिर–परिचित होने चाहिए। रेडियो में समय की मक्रत्ता मुख्य मानी जाती है। कारण कि श्रोता किसी विषय–बिन्दु पर अधिकतम 2 या 3 मिनट तक ही केन्द्रित रह सकते हैं। रेडियो के सन्दर्भ में उच्चरित ध्वनियों की बात करें, तो इस कथन का महत्त्व बहुत अधिक है–"शब्दों में केवल अर्थ ही नहीं होता, ध्वनि भी होती है। ध्वनियों के श्रव्य में भी आनन्द होता है। कविता में तो इस नाद सौन्दर्य का बहुत ही महत्त्वपूर्ण स्थान है, लेकिन उसके लिखित रूप के मौन पाठ द्वारा इस आन्न्द की उपलब्धि नहीं हो सकती।"

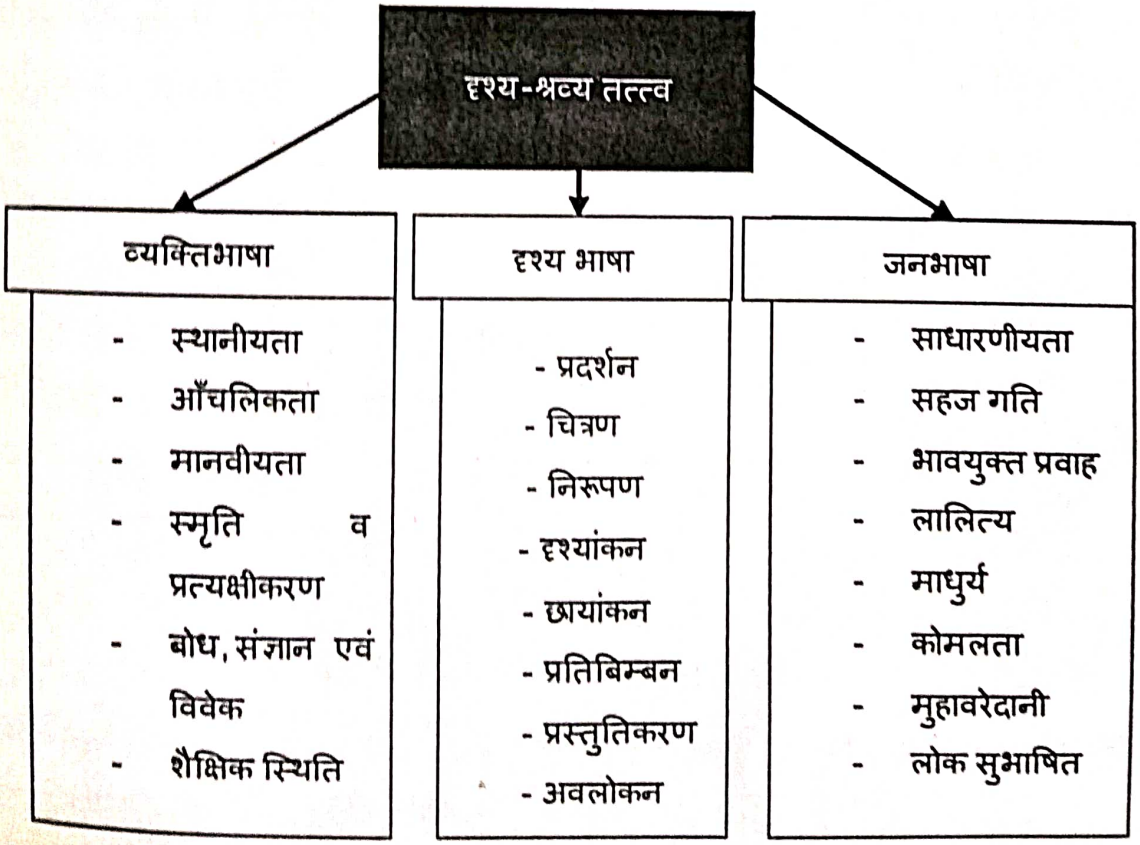


बोलता हुआ आदमी टेलीविजन पर दिखाई देता है। टेलीविज माध्यम की बड़ी खासियत यह है कि वह श्रव्य और दृश्य दोनों माध्यमों से मिलकर बना संयुक्त उपक्रम है। टेलीविज़ माध्यम लेखन की बात करने से पूर्व हम इस तथ्य पर अवश्य ध्यान दें कि हम जो भाशा बोलेंगे वह किसी न किसी साँचे में ढली होंगी, तो वह कैसी हो और किस साँचे में ढले, इसे तय करना भाषा में ही संभव है। टेलीविजन की भाषा अन्य भाषाओं से भिन्न होती है। इस कारण इनके लेखन की प्रक्रिया भी अलग तरीके का होता है। पहले टेलीविज़न माध्यम को एक जनमाध्यम के रूप में देखें, तो इसमें प्रयुक्त भाषा प्रायः मानवीय ऊर्जा से भरपूर होती है। सर्जनात्मक क्षमता और आन्तरिक प्रतिभा का भी टेलीविज़न लेखन के विभिन्न प्रकाश्यों में विशेष योगदान होता है। इस माध्यम लेखन की बड़ी ताकत है इनकी भाषा में उपलब्ध सजीवता एवं विपुलता; जो देखने वाले को खुद से इस तरह 'कनेक्ट' करती हैं मानों उनकी ही छवि–प्रतिछवि का प्रस्तुतिकरण किया जा रहा हो। जनमाध्यम लेखन करने को प्रवृत्त व्यक्ति को यह बात अच्छी तरह समझ लेनी चाहिए कि एकसाथ "बोली और सुनी हुई भाषा में भावाभिव्यंजना की जो शक्ति है, वह लिखी और पढ़ी जाने वाली भाषा में नहीं है। हम जानते हैं कि शब्द हमारी भावनाओं–अनुभतियों के मूर्तिमान रूप हैं? इन्हीं की शक्ति से वे जीवित रहते हैं। शब्दों के उच्चरित रूप को हमारे भाव और विचार ही सजीव एवं प्राणवान बनाए रखते हैं; लेकिन उनके लिखित रूप में यह बात नहीं रह जाती। उन्हें सजीव बनाए रखने वाली हमारी अनुभूतियाँ उनके पीछे से

हट जाती हैं।" दृश्य शक्ति की सार्थकता इस बात में भी है कि–"आँखों और मुखाकृति से वक्ता की अभिव्यंजना शक्ति बढ़ती है। यही बात अन्य भाव–भंगिमाओं एवं संकेतों के सम्बन्ध में कही जा सकती है। हाथ और उंगलियों के इशारों से से भी हम भावाभिव्यक्ति करते हैं; कभी–कभी तो यह भावाभिव्यक्ति इतनी सशक्त होती है कि शब्द उनके समक्ष अत्यंत दुर्बल मालूम पड़ते हैं।"

टेलीविज़न लेखन में श्रव्य–गुणों का होना आवश्यक है। उसके अतिरिक्त दृश्य–शक्ति का होना भी जरूरी है। टेलीविजन व्यक्ति–भाषा, जनभाषा एवं दृष्यभाषा का समूहीकरण कर एक विशाल नेटवर्क का निर्माण करता है। यह निर्माण सदैव जनता के हित और उसके मत की रक्षा करता है।

माध्यम लेखन सम्बन्धी उपर्युक्त अध्ययन–विश्लेषण की अपनी सीमाएँ हैं और व्यक्तिगत बाध्यता भी। अतः निष्कर्ष तौर पर कहे तो, माध्यम लेखन मानवीय कार्यकलापों, अंतःक्रियाओं और मानवोचित सम्बन्धों को जोड़ने में सेतुमार्ग की भूमिका निभाते हैं। भारत में लोकमाध्यमों की परम्परा रही है



जिसे पारम्परिक माध्यम के रूप में जाना, परखा और आजमाया गया है। लोकसमुदाय तक सामूहिक इच्छा–आकांक्षा को संचारित करने में इन माध्यमों की भूमिका महत्त्वपूर्ण रही है जिसका मुख्य उद्देष्य लोक–शिक्षण व जन–जागरण का रहा है। यह भी कि लोकमाध्यमों में सदैव वर्तमान–बोध निहित होता है जिसकी अपेक्षा आधुनिक जनमाध्यमों से की जाती है। आज स्थानीय–वैश्विक विषयवस्तु अथवा घटनाक्रमों के बारे में जानने के लिए माध्यम पर निर्भरता और अभिरुचि दोनों बढ़ी है। मौजूदा समय में माध्यम की भूमिका जनमत–निर्माण और वैचारिकी गढ़ने में सर्वाधिक है, इसलिए माध्यम लेखन की प्रणाली व्यावहारिक व समसामयिक होना अनिवार्य है। माध्यम चाहे प्रिंट हो या इलेक्ट्रॉनिक या कि न्यू मीडिया के संजालों से घिरी वेबोपयोगी नवमाध्यम; इनका लोकदायरा यानी 'पब्लिक स्पियर' से सीधा जुड़ाव है। अतः भारतीयता का मूलभाव और राष्ट्रीयता का आत्मबोध ही माध्यम की सफलता और उसकी गरिमा को अनुकरणीय बना सकता है। विशेषकर माध्यम लेखन सम्बन्धी तथ्य–संग्रह, सामग्री–निर्माण व तत्सम्बन्धी व्याख्या–विश्लेषण में सजगता, सावधानी तथा गंभीरता अत्यन्त आवश्यक है। क्योंकि कागद की लिखी हो या तकनीक से प्रसारित, जनसाधारण के मानस को बनाने और उनको ऊँचा उठाने में जनमाध्यमों की भूमिका सर्वश्रेष्ठ है।

●

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Dr. Sambhu Prasad, Assistant professor, Rajiv Gandhi University, Arunachal Pradesh born and brought up in Jamshedpur, Jharkhand. During his school and college days, he was a good sportsperson. He completed undergraduate, postgraduate and doctoral degree in physical education from the pioneer institute Lakshmibai National Institute of Physical Education, Gwalior. He has been engaged both in teaching and research for more than 10 years in India as well as abroad and has published over 20 research papers in reputed National and International journals. He served as Assistant Professor in Mekelle University, Ethiopia and was also associated with University Coaching Camp in track and field for two years.

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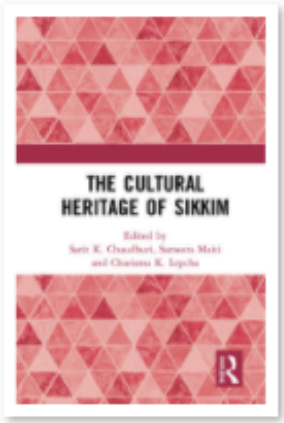

The Cultural Heritage of Sikkim

Edited By ***Sarit K. Chaudhuri, Sameera Maiti, Charisma K. Lepcha***

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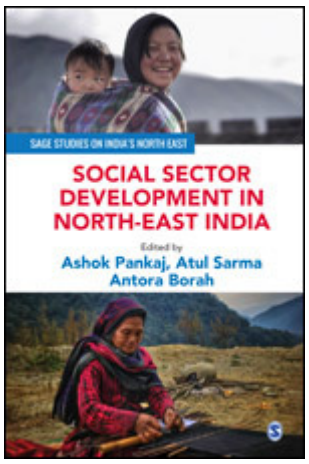

Social Sector Development in North-East India

Edited by:

Ashok Pankaj - Professor and former Director at the Council for Social Development, New Delhi
Atul Sarma - Chairman of the OKD Institute for Social Change and Development, Guwahati
Antora Borah - Research Associate at the Council for Social Development, New Delhi

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Format	Published Date	ISBN	Price
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Social Sector Development in North-east India is the first comprehensive book that makes a strong case for people-centric social sector development of North-east India. This book argues that human capital formation through social sector development should be the strategic goal of development of this region, as the prospect for service sector development is much higher compared to that of the primary and secondary sectors. This needs a course correction in the erstwhile approaches of development, which has been driven by political and strategic considerations such as national security and the territorial integrity of India. This book advances an argument for a shift in approach of development policy from top-down, infrastructure-focused to bottom-up, people-centric and social sector development-focused. It also critiques the mainstream understanding of North-east India that treats it as a geographical entity and a monolithic socio-cultural society, ignoring its rich ethnic diversities, cultural pluralities and regional variations.

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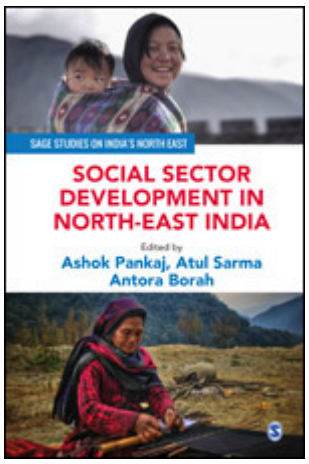

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CHAPTER 8

Flowering Plant Diversity in the Alpine Regions of Eastern Himalaya

DIPANKAR BORAH*, A. P. DAS, SUMPAM TANGJANG, and TONLONG WANGPAN

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ABSTRACT

The Himalayas form a graceful and vast abode of floristic and faunal elements and also represent diverse human cultures spreading through its length and breadth. Eastern Himalayas, a biodiversity hotspot is not only a home to the world's highest mountains but is also amongst the highest diversity rich areas of the world. The easternmost part of the Indian Himalayas harbors many special vegetation types, depending upon altitudinal and climatological stratification. Arunachal Pradesh is one of the richest states in the region in terms of biodiversity, owing to its unique geographical position and altitudinal gradients. The article ventures preliminary account of flowering plant diversity of Nagula wetland complex of Arunachal Pradesh, which has more than 100 alpine freshwater lakes fed by melting snow. The altitude ranges from 3,500–4,500 meters above mean sea level. The study recorded a total of 106 species, falling under 68 genera and 32 families. Asteraceae is the most dominant family followed by Orobanchaceae, Gentianaceae, etc. If the area's natural vegetation is conserved without any disturbance that will maintain not only the pristine beauty but also the rich and original biological elements of the area. A high proportion of angiosperms of this area can be adopted for ornamental gardens, and some others can be tested for their medicinal properties.

Vertika Shukla · Narendra Kumar
Editors

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Status of Medicinal Plants in Context of Arunachal Pradesh

4

Tonlong Wangpan and Sumpam Tangjang

Abstract

The ethnomedicinal use of plants is one of the most successful criteria used by the pharmaceutical industry in finding new therapeutic agents for the various fields of biomedicine. There are more than one-tenth of plant species used in drugs and health products, with more than 50,000 species being used worldwide. Arunachal Pradesh alone has recorded more than 500 species of medicinal plants used by traditional herbal practitioners. These knowledge are generally passed down orally. About 70% of the herbalists are from old generation, which shows that this wisdom in the young generation is degrading fast due to rapid modernization. Unfortunately, medicinal plant resources are being harvested haphazardly in increasing volumes from its native habitat. Recently, various sets of recommendations relating to the conservation of medicinal plants have been developed, such as providing both in situ and ex situ conservation. Also, the policymaker of the state has come up with several plans with an idea of conservation of these plants, such as Herbal Garden, State CAMPA, Demonstration plot, Demonstration plot cum Nursery and MPCA (Medicinal Plants Conservation Area). The plants used in traditional medicines are potential source of therapeutics aids and have significant role in rural healthcare system all over the world. There is a vast scope for Arunachal Pradesh to emerge as a major player in the global herbal product-based medicine, owing to its rich biological resources. Therefore, it requires urgent systematic investigation using biotechnological tools to authenticate and develop new novel drugs from the rich bio-resources of the region.

Keywords

Bioactive compounds · Ethnobotany · Biodiversity · Northeast India

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4.1 Introduction

The ethnomedicine is a complex multidisciplinary system constituting the use of plants, spirituality and the natural environment which has been the source of healing for ages. Research interest and activities in the area of ethnomedicine have increased tremendously in the last decade. Since the inception of the discipline, scientific research in ethnomedicine has made important contribution to the understanding of traditional subsistence, medical knowledge and practice. However, it is interesting to note that the ethnomedicinal use of plants is one of the most successful criteria used by the pharmaceutical industry in finding new therapeutic agents for the various fields of biomedicine. Today about 80% of the world's population rely predominantly on traditional medicinal plants and plant extracts for healthcare. According to data released by the World Health Organization (WHO 2002), ethnomedicine has maintained its popularity in all regions of the developing world, and its usefulness is rapidly expanding in the industrialized countries. The systematic study of medicinal and aromatic plant has been gaining its importance and momentum after the UN Convention on Biological Diversity (1992) wherein due importance has been given for systematic botanical and ethnomedicobotanical researches which include systematic documentation, conservation and sustainable utilization at global level.

WHO Geneva draft guideline on traditional medicine strategy (2004) revealed that 80% of global population depend on herbal medicine, mostly of botanical origin. The declaration further serves as directives to the member nations for systematic research, collection and harvesting of aromatic and medicinal plant resources. Medicinal plants have played an essential role in the development of present healthcare systems. Since many decades, man has relied on traditional medicinal plants for curing and preventing ailments, including the elevation of both physical and spiritual well-being. The use of herbal medicines to treat disease is almost universal among the many tribal societies, and the integrity and healing properties of these herbs were explored and witnessed by several people as well as many researches since ages. Likewise, herbal drugs were basis of Indian and Chinese medicine for millennia. Being considered as one of the 17 mega biodiversity countries of the world, India is rich in its biological resources. It has rich vegetation of more than 50,000 plant species of which about 20,000 plants have medicinal values. However, the traditional practitioners may be using more than the official statistics in preparation of herbal formulation. According to the report of WHO (World Health Organization), 80% of world population still depends on traditional medicines owing to its efficiency, safety, cost-effectiveness and easy accessibility. In this region, most herbal practitioners formulate and dispense their own recipes which seek attention of researchers for proper documentation and scientific intervention. North-eastern part of India, with richest reservoir of diversity of plants, is one of the biodiversity hotspots. Also, this region is known for diversified culture of inhabiting ethnic tribal communities.

The state of Arunachal Pradesh with total geographical area of 83,743km^2 lies in between latitude 26° 30′ N and 29° 30′ N and longitude 91° 30′ E and 97° 30′ E. The entire East Himalayan region including Arunachal Himalaya has been rated as one of the top 12th global biodiversity hotspots. Due to its unique topography, the forest of

Arunachal Pradesh is a hub centre of medicinal and aromatic plants, and the state comprises of all the characteristic vegetation type of the country. The state is also known for its rich and veritable cultural heritage wherein 26 major tribe and 110 subtribe living in close association with nature. The indigenous medicinal knowledge of Arunachal Pradesh has been found to be very rich and diverse among the tribes (Tag and Das 2006). The tribal population of this region possess treasured traditional knowledge since the time immemorial. This knowledge is completely based on their needs, instinct, observation, trials, errors and long-term personal experiences. Further, the traditional knowledge have always been developed, enhanced and passed on from one generation to the next, playing a vital role in the lives of these rural folks. In recent decade, plant-based medicine has gained its popularity worldwide because of their better cultural acceptability, compatibility and lesser side effect in comparison to its allopathic counterpart. The therapeutic activity of these herbs has made a significant contribution in the advancement of several local herbal therapies, but such folk traditional system is waning fast with the impact of modernity. Also, the increasing pressure from un-systemic harvesting, expansion of agricultural land, urbanization and other anthropogenic activities have further exploited the traditional herbal therapies.

4.2 Literature on Status of Medicinal Plants Research in Arunachal Pradesh

Arunachal Pradesh is known for its rich of medicinal plant heritage in nature. Such vast diversity at species level in medicinal plants sector confers scopes for priorities research in the state. Jain (1987) initiated some ethnobotanical research in Arunachal Himalaya. Subsequent documentation work on medicinal and ethnobotanical line was carried out in state by Hajra et al. (1996), wherein they mentioned 76 medicinal plants used by the Monpa tribe of the state. Tag et al. (2008) and Das (1986) reported ethnobotanical heritage of the Adi tribe of East Siang District wherein he also reported some significant medicinal species used by the tribes. The unexplored traditional knowledge relating to the diverse use of medicinal plant need to be documented with methodological rigour. Murtem (2000) reported some 25 species of wild edible plants of Nyishi tribe from Subansiri and Papum Pare District. Tag and Das (2004) documented 28 species of ethnobotanical plant used by Hill Miri (Nyishi) tribe of middle Subansiri which includes medicinal plants used in curing various ailments. Kala (2005) reported ethnomedicinal botany of the Apatani of Subansiri District wherein he mentioned 158 species of medicinal plant distributed across 73 families and 124 genera. Das and Tag (2005) reported 45 species of ethnomedicinal used by the *Khamti* tribe of Lohit District. They have reported five antimalarial plants four species in bone fracture, three species in anaemia and two species in snakebite, cancer, reproductive health and rabies and one plant each in tuberculosis, diabetes and jaundice, and the rest are used for curing different ailments. Hussain and Hore (2008) have mentioned 64 species of medicinal and aromatics plant distributed over 45 genera and 36 families that were collected from 6 districts of Arunachal Pradesh. Sarmah et al. (2008) reported 63 medicinal plant

used by the Chakma community residing in the northwestern periphery of Namdapha National Park in curing various diseases. Kar and Borthakur (2008) dealt with 35 plant species use against dysentery, diarrhoea and cholera from erstwhile undivided Kameng District of Arunachal Pradesh wherein they emphasized on conservation of indigenous plant wealth through commercial cultivation and also for developing new and more efficacious remedies. Tag et al. (2009) highlighted diversity and distribution of ethnomedicinal plant used by the Adi tribe in East Siang District of Arunachal Pradesh, wherein they mentioned 41 species of ethnomedicinal plants belonging to 39 genera clubbed within 28 families that are mostly used in human and animal healthcare system among the rural Adi folk of East Siang District. Sen et al. (2009) reported 37 plant species belonging to 29 families used by Khamptis of Arunachal Pradesh used in traditional healthcare practices. Cut and wound, pain and inflammation caused by the insects and accidental injuries are one of the common ailments faced by the tribes of tropical and subtropical Arunachal Himalaya. In this line, Namsa et al. (2009) reported 34 species of anti-inflammatory plants used by the Khamti tribe of Lohit District. Tag et al. (2009) evaluated anti-inflammatory potential of *Chloranthus* species used by the Khamti tribe through mouse model experiment. Goswami et al. (2009) reported 10 medicinal plant used by Tagin tribe for curing dysentery, while Srivastava (2009) investigated medicinal plants of Adi tribe and reported 108 species of plant used in their day-to-day life. Kato and Gopi (2009) reported 12 species of insect that is used as edible food, but there is no proper documentation of plant species that is used for medicinal purpose in Galo tribe. Kagyung et al. (2010) mentioned 44 plant species belonging to 31 families used in treatment of various gastrointestinal diseases from Arunachal Himalaya. Doley et al. (2010) reported 15 species of lesser known ethnomedicinal plant used by the *Nyishi* community of Papum Pare District, while Shrivastava et al. (2010) appraised various uses of 106 plant species used among the Apatani tribe as food and ethnomedicine and for handicraft, hunting and cultural purposes. Panda and Srivastava (2010) reported new ethnomedicinal uses of seven species of Ericaceae by the people of Aka tribe of Jamiri, Nepalese of Dedza village and Bomdila and Dirang Monpas or Drangangpa of Bomdila in West Kameng District. Tangjang et al. (2011) reported 74 medicinal plants species from Tirap, Lower Dibang Valley and Papum Pare District of Arunachal Pradesh, Eastern Himalayan region. Khongsai et al. (2011) presented their cross-cultural ethnobotanical report on Apatani, Monpa, Sinpho, Nyishi, Tangsa, Padam and Idu tribe of Arunachal Pradesh, but they could quantify the data in quantitative ethnobotanical approach.

4.3 Diversity and Utility of Medicinal Plants in Arunachal Pradesh

More than one-tenth of plant species are used in drugs and health products, with more than 50,000 species being used (Chen et al. 2016). China and India have the highest numbers of medicinal plants used, with 11,146 and 7500 species, respectively (Rafieian-Kopaei 2013). Arunachal Pradesh alone has recorded 5000 species

of angiosperms, of which more than 500 species of medicinal plants are reported from the state (Murtem 2000; Haridasan et al. 2003). Table 4.1 contains some of the important medicinal plants commonly used by the tribal community of this region.

4.4 Practitioners Eminence Knowledge

Traditional knowledge of the remedies is passed down orally, without any written records. About 70% of the herbalists are from old generation, strongly bonded with their traditional knowledge. The traditional wisdom in the young generation of most of the tribes is degrading fast due to the wind of modernization. Younger generations are least concerned about their ancestral wisdom. Herbal practitioners among the tribe being mostly marginal farmers, having very little income from their agriculture produce earn their sustenance partly from selling their herbal preparations. They collect the plants used in herbal preparation mostly collected from the forest. However, some expert practitioners have their own herbal garden. Thus, for such practitioners, the degree of dependence on the forest resources becomes partial.

4.5 Conservation Strategies and Sustainable Management of Medicinal Plants

The local communities are chiefly dependent on the traditional healthcare system, while the medicinal plants required in traditional therapy are mostly confined in the core of forest area. Unfortunately, medicinal plant resources are being harvested haphazardly in increasing volumes from its native habitat, which forced the policymaker to come up with an idea of conservation of these plants. Recently, conservation efforts have been initiated by State Medicinal Plants Board on conservation of endangered and endemic medicinal plants (Fig. 4.1). There are several ongoing projects on such plants including *Coptis teeta*, *Taxus baccata* and *Paris polyphylla* in several locations, while several projects were already completed such as Herbal Garden, State CAMPA, Demonstration plot, Demonstration plot cum Nursery and MPCA (Medicinal Plants Conservation Area). So, the in situ conservation approach of these plants in their local habitat is the need of an hour, before it is too late in our endeavour, with the help of local communities. Also, encouraging the local communities ex situ conservation of these medicinal plants would help them in deriving their livelihood, raising their living standard. Therefore, it is apparent that medicinal plants proffer with the low-cost investment and high-value income generation involving local communities in conserving medicinal plants would be a noble initiative of recent developments in researches.

Various sets of recommendations relating to the conservation of medicinal plants have been developed, such as providing both in situ and ex situ conservation. Natural reserves and wild nurseries are typical examples to retain the medical efficacy of plants in situ (or in their natural habitats), while botanic gardens and seed banks are important paradigms for ex situ conservation.

Table 4.1 Common medicinal plants of Arunachal Pradesh used in preparation of herbal formulation of traditional medicines

Sl. no.	Botanical name	Family	Utility
1.	*Abroma augusta* (L.) L.f.	Rubiaceae	Stomach ache, dysentery and vomiting
2.	*Achyranthes aspera* L.	Amarnanthaceae	Malaria
3.	*Achyranthes bidentata* Blume	Amaranthaceae	Plant is diuretic and astringent
4.	*Aconitum ferox* Wall.	Ranunculaceae	Underground roots and tubers are used in arrow poisoning by local hunters
5.	*Acorus calamus* L.	Araceae	Rhizome is used in respiratory disorders
6.	*Adiantum capillus-veneris* Linn.	Adiantaceae	Plant is used in cough
7.	*Aegle marmelos* Correa	Rutaceae	Fruit is used in diarrhoea and dysentery
8.	*Ageratum conyzoides*	Asteraceae	Blood flow, dysentery and diarrhoea, wound healer, veterinary, fish poison
9.	*Ajuga integrifolia* Buch.-Ham.	Lamiaceae	Malaria
10.	*Alangium alpinum* (C.B. Clarke) W.W. Sm. & Cave	Cornaceae	Used in abdomen of child to deworming
11.	*Allium hookeri* Linn.	Liliaceae	Skin diseases, veterinary, bone fracture
12.	*Allium sativum* Linn.	Liliaceae	Bone fracture and malaria
13.	*Alnus nepalensis*	Betulaceae	Disinfectant, diuretic, reduce swelling, prevent excessive sweating, also used for carpentry
14.	*Aloe barbadensis*	Liliaceae	Burns and cut, applied in face for smoother skin, anti-inflammatory, dermatitis
15.	*Aloe vera* (L.) Burm.f.	Xanthorrhoeaceae	Acid reflux
16.	*Alpinia nigra*	Zingiberaceae	Analgesic, appetizer, antifungal, jaundice, gastric ulcer, diuretic, expectorant, anti- inflammatory
17.	*Alstonia scholaris* (L.) R. Br.	Apocynaceae	Snakebite, skin diseases, malaria and inflammation
18.	*Amaranthus spinosus* L.	Amaranthaceae	Stomach ache, constipation
19.	*Amomum subulatum* Roxb.	Zingiberaceae	Fruit is used in cough and stomachic disorders
20.	*Andrographis paniculata* (Burm. f.) Nees.	Acanthaceae	Malaria
21.	*Anthocephalus chinensis* (Lam.) A. Rich. Ex. Wall.	Rubiaceae	Plant is used as tonic in dysentery and spleen disorders
22.	Argyreia nervosa	Convolvulaceae	Malaria

(continued)

Table 4.1 (continued)

Sl. no.	Botanical name	Family	Utility
23.	Argyreia nervosa (Blume.) Boj.	Convolvulaceae	Rheumatism and as tonic, wounds and malaria
24.	*Arisaema consanguineum*	Araceae	Locally used for arrow poisoning for hunting
25.	*Artemisia nilagirica*	Asteraceae	In headache and stomach pain, used as vegetable, to get relief from asthma
26.	*Artemisia indica* Willd.	Asteraceae	Malaria
27.	*Artemisia nilagirica* (Clarke) Pamp.	Asteraceae	Wounds, cuts, scabies and inflammations
28.	*Artemisia vulgaris* L.	Asteraceae	Root is used as tonic; plant is used as anthelmintic
29.	*Arundina graminifolia* (D.Don) Hochr.	Orchidaceae	Intestinal biliary colic, abdominal pain
30.	*Asplenium phyllitidis*	Aspleniaceae	Antioxidant, antimicrobial, locally used for decoration in local festival
31.	*Azadirachta indica* A. Juss	Meliaceae	Stomach disorder, diarrhoea and malaria
32.	*Baliospermum calycinum*	Euphorbiaceae	Purgative, stimulant, antidote in snakebite, asthma, jaundice, gastric problem, gout and rheumatism, toothache
33.	*Bambusa tulda*	Poaceae	Bamboo shoots are consumed as integral part of diet
34.	*Bauhinia purpuea* L.	Caesalpiniaceae	Stem bark is used in throat disorder, worm infestation
35.	*Bauhinia variegata*	Fabaceae	Asthma, ulcer, digestive problem, antioxidant, locally also used as spies
36.	*Begonia josephii* A. DC.	Begoniaceae	Dysentery
37.	*Berberis aristata* DC	Berberidaceae	Root bark is used in diabetes, jaundice and leucoderma
38.	*Bidens pilosa* Linn.	Asteraceae	Wounds and skin inflammations
39.	*Blumea adamsii* J.-P. Lebrun & Stork	Compositae	Constipation
40.	*Bombax ceiba* L.	Bombaxaceae	Root and stem bark are aphrodisiac, stimulant
41.	*Brassica campestris* Linn.	Brassicaceae	Oil from seed along with ginger, turmeric, garlic used in various ailments
42.	*Brassica rapa* L.	Brassicaceae	Bladder inflammation
43.	*Bryophyllum adelae* (Hamet) A.Berger	Crassulaceae	Dysentery
44.	*Bryophyllum calycinum* Salisb.	Crassulaceae	Leaf juice is used in kidney stone and urinary disorders
45.	*Buddleja asiatica* Lour.	Scrophulariaceae	Diarrhoea, beverages fermentation

(continued)

Table 4.1 (continued)

Sl. no.	Botanical name	Family	Utility
46.	Calamus inermis	Arecaceae	Malaria
47.	*Callicarpa arborea*	Verbenaceae	Insect repellent, skin diseases, scorpion sting, also used in toothache
48.	*Callicarpa macrophylla* Vahl	Verbenaceae	Fruit is used in blood dysentery and skin diseases
49.	*Calotropis gigantea* (L.) R.Br. ex Ait	Asclepiadaceae	Flowers are used in cough; root as *Rasayana*
50.	*Campylandra aurantiaca Wall*	Liliaceae	Indigestion
51.	*Cannabis sativa* L.	Cannabinaceae	Plant leaf is used in digestion and dysentery
52.	*Cannabis sativa*	Cannabaceae	Stomach disorder, hypnotic, sedative, anti- inflammatory, analgesic, nausea, vomiting, hallucinogenic
53.	*Carica papaya* L.	Caricaceae	Malaria and gastric
54.	*Cassia alata* L.	Caesalpiniaceae	Leaf is used in ring worm; leaf decoction is used in bronchitis and asthma
55.	*Cassia fistula* Linn.	Caesalpiniaceae	Leaves and seeds are laxative. Leaf juice is used in skin diseases
56.	*Cassia tora* Linn.	Caesalpiniaceae	Leaf paste and oil are used in skin diseases
57.	*Centella asiatica* (L.) Urban	Apiaceae	Plant is used in arthritis, diabetes, blood disorders and brain tonic
58.	*Cephalanthus occidentalis* L.	Caesalpiniacae	Plant is digestive and used in skin diseases, fever and cough
59.	Chenopodium album	Chenopodiaceae	Locally used in preparing local wine and also eat as a vegetable
60.	*Chromolaena odoratum*	Asteraceae	Wound healing, relieve pain, anti-gonorrheal, diuretic, skin disease
61.	*Chrysanthemum indicum*	Compositae	Chest pain, prostate cancer, antidiabetic, stomach ache, fever, dysentery, cold, swelling
62.	*Cinnamomum camphora* Nees Eberm.	Lauraceae	Leaf is useful in diarrhoea and skin diseases
63.	*Cinnamomum tamala* Nees Eberm.	Lauraceae	Leaf is used in cough, digestion and diabetes
64.	*Cissampelos pareira* L.	Menispermaceae	Root is bitter, diuretic and useful in fever and dysentery
65.	*Citrus indica* Tanaka.	Rutaceae	Face pimples removal
66.	*Citrus limon* L. *(Linn.) Burm.*	Rutaceae	Dysentery, dehydration and stomachic trouble and liver problem
67.	*Citrus maxima* (Burm.) Merrill.	Rutaceae	Fruit is digestive and cardiotonic

(continued)

Table 4.1 (continued)

Sl. no.	Botanical name	Family	Utility
68.	*Citrus medica*	Rutaceae	Treatment of scurvy, intestinal ailments, antidote, anticancer, weak eyesight, vomiting, skin diseases, haemorrhoids
69.	*Citrus reticulata* Blanco	Rutaceae	Fruit juice is used in rheumatism, fever, blood disorder and digestion
70.	*Citrus sinensis* (L.) Osbeck	Rutaceae	Kidney stone problem
71.	*Clerodendrum colebrookianum* Walp.	Verbenaceae	High blood pressure, stomach disorder, headache
72.	*Clerodendrum glandulosum* Lin dl.	Lamiaceae	Malaria
73.	*Clerodendrum serratum* (Linn.) Moon	Verbenaceae	Root is useful in malaria
74.	*Colocasia esculenta*	Araceae	Fever and cough, petiole juice is used as styptic and stimulant
75.	*Coptis teeta Wall.*	Ranunculaceae	Malaria, fever, jaundice, stomach ache, liver diseases, hypertension and diabetes
76.	*Costus speciosus (Keon.) Sm.*	Zingberaceae	Rhizome is used as worm repellent and blood purifier
77.	*Crassocephalum crepidioides*	Asteraceae	Antimalarial, analgesic, epileptic, wound bleeding, headache
78.	*Crotolaria juncea* L.	Fabaceae	Seeds, leaves are used in insanity, fever with catarrhal
79.	*Curcuma caesia* Roxb.	Zingibaraceae	Rituals and pimple removal
80.	*Curcuma longa* L.	Zingiberaceae	Stomach ache
81.	*Cyclosorus parasiticus*	Thelypteridaceae	Gout and rheumatism, anthelmintic, antifungal and antibacterial
82.	*Datura stramonium* L.	Solanaceae	Leaves are used as narcotic, sedative and diuretic
83.	*Debregeasia longifolia*	Urticaceae	Antitumours, rheumatism; juice is applied to the areas of the skin affected by scabies
84.	*Dendrocalamus strictus Nees.*	Poaceae	Wound or cut
85.	*Dillenia indica* Linn.	Dilleniaceae	Fruit is used to improve appetite, heart fever, cough and mouth disease
86.	*Dioscorea alata* Linn.	Dioscoreaceae	Gastritis
87.	*Dioscorea bulbifera* L.	Dioscoreaceae	Root is aphrodisiac and tonic
88.	*Dioscorea floribunda*	Dioscoreaceae	Intestine diverticulosis, gall bladder pain, for increasing, energy, rheumatoid arthritis
89.	*Dioscorea pentaphylla* L.	Dioscoreaceae	Root is aphrodisiac and tonic
90.	*Drymaria cordata* (L.) Willd. ex Schult.	Caryophyllaceae	Vomiting

(continued)

Table 4.1 (continued)

Sl. no.	Botanical name	Family	Utility
91.	*Drymaria diandra* Blume	Caryophyllaceae	Plant juice is laxative and ant febrile
92.	*Elaeocarpus floribundus* Blume	Elaeocarpaceae	Bark and leaf infusion is used as mouth wash for inflamed gums. Fruit is rich source of vitamin C and digestive
93.	*Eleusine coracana*	Poaceae	Cough, cold, congestion, antimicrobial, anti- inflammatory, food preservative
94.	*Elaeocarpus floribundus*	Elaeocarpaceae	Fruits have medicinal properties
95.	*Embelia ribes* Burm. f.	Myrsinaceae	Fruit and root used in worm infestation, liver disorders and as tonic
96.	*Emblica officinalis*	Euphorbiaceae	Liver tonic, antidiabetic, asthma, peptic ulcer, analgesic, heart problems, jaundice
97.	*Erigeron bonariensis*	Asteraceae	Vapour of leaves is inhaled in sinus problem
98.	*Eryngium foetidum* L.	Apiaceae	Dysentery
99.	*Erythrina stricta roxb.*	Fabaceae	Scorpion sting, gout, anti-inflammatory, anxiolytic property
100.	*Euphorbia ligularis roxb.*	Euphorbiaceae	Bone fracture, arrow poisoning, antiarthritis, purgative, asthma, expectorant
101.	*Fagopyrum esculentum* Moench	Polygonaceae	Stomach ache
102.	*Ficus cordata* (Thunb.)	Moraceae	Dysentery
103.	*Ficus glomerata* Roxb.	Moraceae	Diabetes and common fodder
104.	*Garcinia pedunculata* Roxb.	Clusiaceae	Leaves used in dysentery and cough
105.	*Gerbera piloselloides*	Compositae	Treat cold, fever, acute conjunctivitis, rheumatic pain
106.	*Gmelina arborea*	Lamiaceae	Purify blood, stomach trouble, leprosy, diuretic, anaemia, snakebite and scorpion sting, ulcers
107.	*Gnaphalium affine*	Asteraceae	Treatment of common cold, antimicrobial
108.	*Gonostegia hirta* (Blume ex Hassk.) Miq.	Urticaceae	Gastric problem, constipation
109.	*Gymnocladus assamicus* Kanjilal.	Fabaceae	Detergent (soap), religious and veterinary
110.	*Gynocardia odorata* R.Br.	Flocourtiaceae	Fruit is used in tooth ailment
111.	*Gynura crepidioides* (BTH.) Moore.	Asteraceae	Vegetables and stomach disorder
112.	*Hedychium gracile*	Zingiberaceae	Mosquito repellent, antifungal, also used as spies

(continued)

Table 4.1 (continued)

Sl. no.	Botanical name	Family	Utility
113.	*Hedychium aureum* C.B. Clarke & H. Mann ex Baker	Zingiberaceae	Liver problem
114.	*Hedychium coccineum*	Zingiberaceae	Cure asthma and indigestion, antimicrobial, also used for local ornamental purposes
115.	*Hedyotis scandens* Roxb.	Rubiaceae	Gastritis, beverages fermentation
116.	*Hibiscus fragrans* Roxb.	Malvaceae	Paste of leaves/flowers used in hair fall/ dandruff problem
117.	*Houttuynia cordata* Thunb.	Saururaceae	Stomach ache, diarrhoea and deworming
118.	*Hydrocotyle sibthorpioides* (Lam.)	Apiaceae	Dysentery
119.	*Laggera pterodonta*	Asteraceae	Anthelmintic, treatment in inflammation and swelling
120.	*Leucas aspera* Spreng.	Lamiaceae	Cuts and wounds, earache, inflammation
121.	*Lindera neesiana* (Wallich ex Nees) Kurz.	Lauraceae	Anthelmintic, diarrhoea, scabies, vegetable oils
122.	*Litsea cubeba* (Lour) Pers.	Lauraceae	Condiments, eczema, heart disease and stomach disorder
123.	*Litsea polyantha*	Lauraceae	Antidepressant, bruises, anti-infertility, cytotoxic, antifungal, insecticide, antiseptic
124.	*Macaranga denticulata*	Euphorbiaceae	Skin damage, antibacterial, fungal infection, wound healing, stomach pain
125.	*Mentha arvensis*	Lamiaceae	Stomach disorder, influenza, appetizer, gall bladder problems
126.	*Mikania scandens*	Asteraceae	Blood clotting, insect bites and sting, antifungal, gastric ulcer, locally used as ornamental plant
127.	*Mimosa pudica*	Mimosaceae	Antidepressant, anticonvulsant, antifertility, sinus, dysentery, tumour, insomnia, antidote in snake poison
128.	*Momordica charantia* Linn.	Cucurbitaceae	Anthelmintic, diabetes
129.	*Moringa oleifera*	Moringaceae	In liver disorder, water purification, etc.
130.	*Mucuna pruriens*	Fabaceae	Parkinson's disease, antiepileptic, antidote in snakebite, in the treatment of itching
131.	*Murraya paniculata*	Rutaceae	Analgesic, antidiarrhoea, anti-inflammatory
132.	*Musa acuminate*	Musaceae	In anaemia, diarrhoea, constipation, ulcer, for menstrual cramps
133.	Musa balbisiana	Musaceae	Blood dysentery, diarrhoea

(continued)

Table 4.1 (continued)

Sl. no.	Botanical name	Family	Utility
134.	*Musa sapientum* L.	Musaceae	Dysentery, urinary problems
135.	*Musa sapientum*	Musaceae	Boiled unripe fruits are given during dysentery, diabetes, anaemia
136.	*Mussaenda glabra* Vahl	Rubiaceae	Constipation
137.	*Mussaenda roxburghii*	Rubiaceae	Detoxify mushroom poison, antipyretic, diuretic, treat blemishes on tongue, acute gastroenteritis
138.	*Mycetia longifolia*	Rubiaceae	Pain relief, ulcer, wound healing, inflammation, antinociceptive
139.	*Ocimum sanctum* Linn.	Lamiaceae	Stomach disorder, inflammations, wounds, cuts
140.	*Ocimum tenuiflorum* L.	Lamiaceae	Gastric problem and malaria
141.	*Opuntia monacantha* (Willd.) Haw.	Cactaceae	Dysentery
142.	*Oroxylum indicum*	Bignonaceae	Cancer, antimalarial, jaundice, anti-arthritic, diarrhoea, fever, ulcer, anti-inflammatory
143.	*Oroxylum indicum* (L.) Kurz.	Bignoniaceae	Malaria and jaundice
144.	*Oxalis corniculata*	Oxalidaceae	Dyspepsia, bowel disorder, anaemia, scurvy, cure opacity of cornea
145.	*Oxalis corniculata* L.	Oxalidaceae	Dysentery
146.	*Oxalis debilis* Kunth	Oxalidaceae	Gastric problem
147.	*Oxyspora paniculata*	Melastomataceae	Treatment of various liver disorder, stomachic, antidote against snake poisoning
148.	*Paederia foetida* L.	Rubiaceae	Stomach ache, gastric, indigestion
149.	*Perilla ocymoides*	Lamiaceae	Locally used as spices or as a curry, in treatment of asthma, also used for nausea, sunstroke, reduce muscle spasms
150.	*Persicaria barbata* (L.) H.Hara	Polygonaceae	Constipation
151.	*Phlogacanthus curviflorn*	Acanthaceae	Boiled leaf juice are used to cure cough and fever
152.	*Phlogacanthus thyrsiflorus*	Acanthaceae	Expectorant, asthma, stomach problems, fever
153.	*Phrynium capitatum*	Marantaceae	Antidiabetic, analgesic, anti-hyperglycaemic, locally used as wrapping and packaging materials
154.	*Physalis minima*	Solanaceae	Gastric trouble, laxative, diuretic, anticancer, in hypertension, anti-inflammatory

(continued)

Table 4.1 (continued)

Sl. no.	Botanical name	Family	Utility
155.	*Piper betel*	Piperaceae	Leaf after rubbing with mustard oil and warming over burning charcoal is applied to belly during stomach ache of children
156.	*Piper longum* L.	Piperaceae	Malaria
157.	*Piper pedicellatum* C. CD.	Piperaceae	Stomach ache, dysentery
158.	*Plantago erosa*	Plantaginaceae	Constipation, improves digestion, astringent, demulcent, diuretic, expectorant, anti-inflammatory
159.	*Plantago major* Linn.	Plantaginaceae	Wounds, inflammations, veterinary
160.	*Polygonum hydropiper* Linn.	Polygonaceae	Fish poison
161.	*Pouzolzia bennettiana* Wight.	Urticaceae	Stomach disorder
162.	*Pouzolzia hirta* Blume ex Hassk.	Urticaceae	Acidity, gastric, appetizer
163.	*Pouzolzia viminea*	Urticaceae	Bleeding, sore
164.	*Psidium acranthum* Urb.	Myrtaceae	Diarrhoea
165.	*Psidium guajava* Linn.	Myrtaceae	Diarrhoea, cough
166.	*Punica granatum* Linn.	Punicaceae	Stomach ache and diarrhoea
167.	*Rauvolfia serpentine*	Apocynaceae	Antihypertensive, sedative, hypnotic, liver ailments, constipation, epilepsy, schizophrenia
168.	*Rhododendron arboreum* Smith. Gurans	Ericaceae	Dysentery, diarrhoea, throat clearance when fish bones get stuck in the gullet
169.	*Ricinus communis* L.	Euphorbiaceae	Abdominal pain
170.	*Rotheca serratum* (L.) Steane & Mabb.	Verbenaceae	Constipation
171.	*Rubia manjith Roxb.*	Rubiaceae	Used to cure headache, cough, cold, locally used as a textile dye
172.	*Rubus acanthophyllos* Focke	Rosaceae	Liver problem
173.	*Saccharum officinarum* Linn.	Poaceae	Jaundice and malaria
174.	*Sapium baccatum*	Euphorbiaceae	Analgesic, antimicrobial, skin irritant, locally used as fish poison
175.	*Saurauia armata* Kurz. Syn.	Saurauiaceae	Leaves applied on the wounds
176.	*Schima wallichii* (DC.) Korth.	Theaceae	Seeds used in stomach trouble

(continued)

Table 4.1 (continued)

Sl. no.	Botanical name	Family	Utility
177.	*Scoparia dulcis*	Plantaginaceae	Jaundice, diabetes, antioxidant, diuretic, analgesic, anti-inflammatory
178.	*Senna tora* (L.) Roxb.	Leguminosae	Liver problem
179.	*Sida rhombifolia* (L.) Raf.	Malvaceae	Gastric problem
180.	*Solanum abancayense* Ochoa	Solanaceae	Constipation
181.	Solanum indicum	Solanaceae	Ringworm, gout, asthma, diuretic, stimulant, expectorant, toothache
182.	*Solanum indicum* Linn.	Solanaceae	Anthelmintic, beverages fermentation
183.	*Solanum khasianum*	Solanaceae	Root decoction is used to treat malaria, antifertility property, anti-inflammatory
184.	*Solanum kurzii*	Solanaceae	Appetizer, toothache, roughage, berry is given to patient of stone problem
185.	*Solanum nigrum* L.	Solanaceae	Diarrhoea
186.	*Solanum spirale Roxb.*	Solanaceae	Stomach ache and indigestion
187.	*Solanum torvum* Sw.	Solanaceae	Stomach ache, spleen problem and anthelmintic
188.	*Solanum xanthocarpum* Burm. f.	Solanaceae	Dental problem
189.	*Spilanthes oleracea* Murr.	Asteraceae	Stop bleeding, skin infections and gastritis, fish poison
190.	*Spilanthes paniculata Wall.*	Asteraceae	Toothache
191.	*Spilanthes acmella*	Asteraceae	Antimalarial, antipyretic, analgesic, flowers are chewed during toothache
192.	*Spondias radlkoferi* Donn. Sm	Anacardiaceae	Dysentery
193.	*Stellaria media* (Linn.) Vill.	Caryophyllaceae	Paste of crushed plant used to stop bleeding
194.	*Stephania japonica* Miers.	Menispermaceae	Stem used in dysentery, leaves in malarial fever
195.	*Sterculia hamiltonii* (Kuntze) Adelb. Syn.	Sterculiaceae	Ayurvedic preparations have medicinal uses
196.	*Stevia suaveolens* Lag.	Compositae	Stomach ache
197.	*Swertia chirayita*	Gentianaceae	Plant decoction is taken in fever, anti-hepatitis B
198.	*Syzgium cumini*	Myrtaceae	Astringent, carminative, antidiabetic, stomach disorder, diarrhoea and dysentery
199.	*Tacca integrifolia*	Dioscoreaceae	Skin disease, leprosy, wound healing, stomach pain, dysentery

(continued)

Table 4.1 (continued)

Sl. no.	Botanical name	Family	Utility
200.	*Terminalia bellerica Roxb.*	Combretaceae	Cold, cough, fever
201.	*Terminalia chebula* Retz.	Combretaceae	Malaria
202.	*Terminalia myriocarpa*	Combretaceae	Bark extract is given in chest pain and as cardiac stimulant
203.	*Thalictrum foliolosum* DC.	Ranunculaceae	Decoction of root used in fever and eye diseases
204.	*Thunbergia grandiflora* (Roxb. ex Rottl.) Roxb.	Acanthaceae	Gastric problem
205.	*Tinospora cordifolia* Miers.	Menispermaceae	Stem used in stomach trouble, dysentery and skin diseases
206.	*Zanthoxylum rhetsa DC*	Rutaceae	Jaundice, wart
207.	*Zanthoxylum armatum*	Rutaceae	Seed and bark are used as tonic during fever and cholera, stomach disorder
208.	*Zanthoxylum hamiltonianum Wall.*	Rutaceae	Malaria
209.	*Zanthoxylum nitidum* (Roxb.) DC.	Rutaceae	Gastric problem
210.	*Zanthoxylum oxyphyllum* Edgew.	Rutaceae	Stomach ache
211.	*Zingiber officinale* Rosc.	Zingiberaceae	Cough and stomach ache
212.	*Zingiber zerumbet (L) Smith*	Zingiberacea	Stomach ache, vomiting, diarrhoea, cough

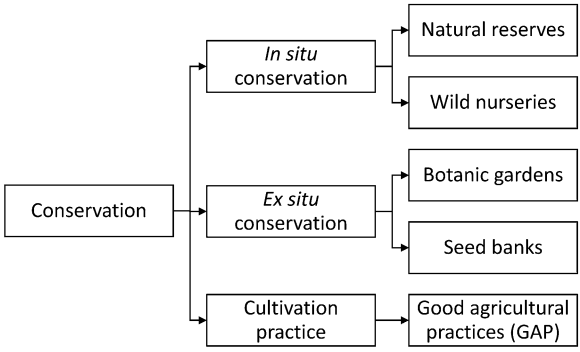

Fig. 4.1 Methodological systems involved in the conservation of medicinal plant

In situ conservation of whole communities allows us to protect indigenous plants and maintain natural communities, along with their intricate network of relationships. It also increases the amount of diversity that can be conserved and

strengthens the link between resource conservation and sustainable use. However, the successful in situ conservation depends on rules, regulations and potential compliance of medicinal plants within growth habitats. Some of the best examples of in situ conservations are natural reserves and wild nurseries. Natural reserves are protected areas of important wild resources created to preserve and restore biodiversity. On the other hand, a wild nursery is established for species-oriented cultivating and domesticating of endangered medicinal plants in a protected area, natural habitat or a place that is only a short distance from where the plants naturally grow.

Ex situ conservation is not always sharply separated from in situ conservation, but it is an effective complement to it, especially for those overexploited and endangered medicinal plants with slow growth, low abundance, and high susceptibility to replanting diseases. It aims to cultivate and naturalize threatened species to ensure their continued survival and sometimes to produce large quantities of planting material used in the creation of drugs, and it is often an immediate action taken to sustain medicinal plant. Some of the good examples of ex situ conservation includes botanic gardens and seed bank. Botany garden maintains the ecosystems to enhance the survival of rare and endangered plant species. It involves a wide variety of plant species grown together under common conditions and often contain taxonomically and ecologically diverse flora. On the other hand, seed banks offer a better way of storing the genetic diversity of many medicinal plants ex situ than through botanic gardens and are recommended to help preserve the biological and genetic diversity of wild plant species.

Apart from in situ and ex situ, cultivation of medicinal plants will provide the opportunity to use new techniques to solve problems encountered in the production, such as toxic components, pesticide contamination, identification error, etc. It can improve the yields of active compounds and ensures the stability of production.

4.6 Conclusion

The plants used in traditional medicines are potential source of therapeutics aids and have significant role in rural healthcare system all over the world. There is a vast scope for Arunachal Pradesh to emerge as a major player in the global herbal product-based medicine, owing to its rich biological resources. The medicinal plants sector provides employment and income opportunities for a large number of indigenous folk in this region. The rich traditional knowledge spawning in this region should be given priority for better utilization of the available resources. However, there is a need of detail study of the medicinal plants used by the community with possible phytochemical investigation. Such investigation may further highlight the true value of these plant species so that they can be managed and conserved for the benefit of the local community in particular and for the welfare of mankind in general. Therefore, it requires urgent systematic investigation using biotechnological tools to authenticate and develop new novel drugs from the rich bio-resources of the region. Scientific approach for their exploration, utilization, conservation and value

addition may be the key points for entrepreneurship development by exploiting the indigenous knowledge on medicines.

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Impact of Noise Levels on SVM-GMM Based Speaker Recognition System

Renu Singh, Utpal Bhattacharjee, Arvind Kumar Singh, and Madhusudhan Mishra

Abstract Speaker recognition is one of the most popular voice biometric techniques used for security reasons in many areas like the banking system, online-shopping, database access, etc. The Speaker recognition system (SRS) works very well in noise-free environments as compared to noisy environments. In this study, the impact of noise levels has been studied by the application of support vector machine-Gaussian mixture model (SVM-GMM) based speaker recognition system. It has been observed that the recognition accuracy improves beyond SNR equals 10 dB with the use of the proposed hybrid system.

Keywords Speaker recognition system · Support vector machine-Gaussian mixture model · Mel-frequency cepstral coefficients · Signal-to-noise ratio

1 Introduction

Speaker recognition is the procedure of recognizing the voice of a speaker by utilizing explicit information encompassed in voice samples [1, 2]. The methodology can be used to verify the claimed identity of people for accessing the systems and enabling

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access control over various services by recognizing the voice. The various applications of the speaker recognition system are voice dialing, phone banking, phone shopping, database access, information and reservation facilities, voice mail, data security control, and remote access of PCs. The other significant use of this technology of speaker recognition is its utilization for criminological purposes [3].

Speaker recognition can be characterized into a number of classes, for example, open and closed set, speaker identification and speaker verification, text-dependent, and text-independent [4]. The recognition of a speaker using a machine comprises the extraction of features, modeling of speaker, and its testing [5]. The estimation of the specific features of the speaker from the speech signal is done using feature extraction. Thereafter, the speaker model is trained with the use of these features. Finally, in the stage of testing, recognition of the speaker is performed by matching with the pattern. The objective of the present work is to investigate the effectiveness of the speaker recognition system accuracy in different noise levels.

2 Speech Parameterization

The inspiration behind the speech parameterization for speaker recognition is to find the phonetic-discriminative attributes of voice signals while neglecting the untrustworthy parts. The best parametric illustration of acoustic waves can be obtained to create a superior performance of a recognition system. The proficiency of this stage influences the activity of the consequent phases. The importance of cepstral features particularly the mel-cepstral for speaker recognition has been studied by many researches [6, 7]. In spite of several limitations, in practical applications using the cepstral features due to high sensitivity in the channel and background noises [8]. Mel-frequency cepstral coefficients are the widely used feature both in speech and speaker recognition systems. Figure 1 represents the block diagram of Mel-frequency cepstral coefficients feature extraction process [9, 10].

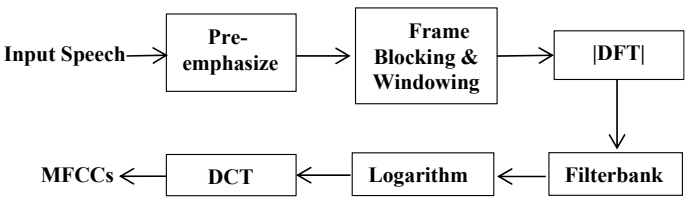

Fig. 1 MFCC feature extraction process

3 Database and Experimental Setup

In this work, the NIST 2003 SRE dataset of clean speech has been used. The voice samples are mixed with various kinds of noises ranging from 0 to 20 dB with an interval of 5 dB signal-to-noise ratio. The AURORA databases are used in preparing the sound noises. The different types of additive noises such as airport, car, exhibition, restaurant, street, and train are added to the clean database of NIST 2003. The following parameters viz. hamming window of length 20 ms, the frame rate of 1600 Hz with 0.97 pre-emphasis factors are considered for analyzing the speech signals. Apart from this for the computation of MFCC features 22 channel filter bank and cepstral features of 14-dimension with cepstral coefficients ranging from c_1 to $c_{13}$are used in this analysis. In order to achieve the final feature dimension of 39, the derivatives of the first- and second-order are added with the base features.

4 Hybrid Speaker Modeling

In this work support vector machine cum Gaussian mixture model has been used. The structure of SVM and GMM-UBM framework was performed in three phases, i.e., training the data using Support Vector Machine (SVM) classifier, building a Universal Background Model (UBM) as well as the speaker models. A gender-dependent 1024 component GMM-UBM has been offline trained for the used dataset considering expectation-maximization algorithm with 100 iterations.

5 Results and Discussion

The performance of a speaker recognition system is degraded in the presence of noisy conditions due to the acoustic mismatch between trained and testing conditions. The influence of noise levels at different noisy environments on SVM-GMM hybrid speaker recognition system is calculated using equal error rate (EER), detection cost function (DCF), and recognition accuracy. The estimation of the EER value of an SRS system depends on the computation of log-likelihood ratio (LLR) scores. Generally, a large number of testing samples are required for the evaluation of false reject rate (FRR) and false alarm rate (FAR), so that the EER can be determined. The DCF is determined as a weighted sum of the two error probabilities and the recognition accuracy as [11]:

$$\text{DCF} = C_{\text{miss}} P_{\text{miss}} P_{\text{target}} + C_{\text{false alarm}} P_{\text{false alarm}} \left(1 - P_{\text{target}}\right)$$

$$\text{Recognition accuracy}(\%) = 100 - \text{EER}$$

The percentage EER values of SVM-GMM and GMM based speaker recognition systems in clean conditions are shown in Table 1. Table 2 represents the individual and average EER value of SVM-GMM based speaker recognition system at 0, 5, 10, 15, and 20 dB signal-to-noise ratios in various noisy environments viz. airport, car, exhibition, restaurant, street, street, and train noises, respectively. From the results, it has been observed that the impact of noise levels is varying for noisy environments. From the table, it is seen that at 0 dB noise level, the percentage equal error rate (% EER) is observed to be lowest for the street which equals 19.88, whereas the highest % EER has been obtained for exhibition noise and equals 26.80. It can also be seen that the percentage of EER is maximum at 5 dB for all the noises considered, and it decreases with an increase in SNR in the range of 10–20 dB. The values of DCF calculated falls in the range of 0.18–0.45.

The recognition accuracy percentage of SVM-GMM based speaker recognition systems at different noise levels and at different noisy environments are calculated and presented in Table 3. The recognition accuracy increases with an increase in SNR in the range of 5–20 dB considered in the study. The comparison of recognition accuracy of SVM-GMM based speaker systems of noisy environments with clean environments is shown in Table 4. The recognition accuracy percentage is seen to be closer for airport and restaurant when compared to a clean environment at 20 dB SNR.

Detection tradeoff function (DET) plots are attained considering the probabilities between "miss" and "false alarm" on a normal-deviate scale for all trials. Figures 2, 3, 4, 5, 6, and 7 show the DET plots between clean vs. noise at various noise levels. Figure 2 reveals that the pattern of DET plot is similar for all noise levels. Figure 3

Table 1 EER value of GMM and SVM-GMM based speaker recognition system in clean condition

Baseline system	Condition	EER (%)	DCF	Recognition accuracy (%)
GMM [12]	Clean	7.02	0.05	92.98
SVM-GMM	Clean	4.12	0.04	95.87

Table 2 EER (%) value of SVM-GMM based speaker recognition system at different noise levels and different noisy environments

Noise types	0 dB		5 dB		10 dB		15 dB		20 dB	
	EER	DCF	EER	DCF	EER	DCF	EER	DCF	EER	DCF
Airport	20.62	0.24	22.68	0.27	17.52	0.18	14.43	0.15	9.27	0.09
Car	19.59	0.23	23.71	0.29	23.71	0.29	18.55	0.19	11.34	0.11
Exhibition	26.80	0.31	22.68	0.27	21.64	0.23	17.52	0.45	10.30	0.40
Restaurant	19.59	0.23	25.77	0.33	22.68	0.23	17.52	0.18	9.27	0.40
Street	19.58	0.22	23.71	0.29	19.58	0.29	19.58	0.29	11.34	0.40
Train	25.77	0.33	25.77	0.33	25.77	0.33	20.61	0.24	12.37	0.12
Average	21.99	0.26	24.05	0.30	21.82	0.27	18.04	0.25	10.65	0.25

Table 3 Recognition accuracy (%) of SVM-GMM based speaker recognition system at different noise levels and environments

Noise types	0 dB	5 dB	10 dB	15 dB	20 dB
Airport	79.38	77.32	82.48	85.57	90.73
Car	80.41	76.29	76.29	81.45	88.66
Exhibition	73.20	77.32	77.23	82.48	89.70
Restaurant	80.41	74.23	74.23	82.48	90.73
Street	80.42	76.29	76.29	80.48	88.66
Train	74.23	74.23	74.23	79.39	87.63
Average	78.00	75.94	76.79	81.97	89.35

Table 4 Recognition accuracy (%) difference of SVM-GMM based speaker recognition system between clean versus noisy environments at different noise levels

Noise types	0 dB	5 dB	10 dB	15 dB	20 dB
Airport	16.49	18.55	13.39	10.30	5.14
Car	15.46	19.58	19.58	14.42	7.21
Exhibition	22.67	18.55	18.55	13.39	6.17
Restaurant	15.46	21.64	21.64	13.39	5.14
Street	15.45	19.58	19.58	15.39	7.21
Train	21.64	21.64	21.64	16.48	8.24
Average	17.86	19.92	19.06	13.89	6.52

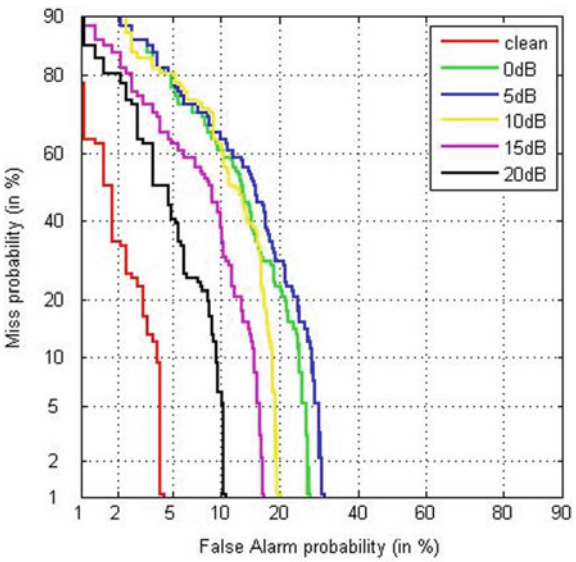

Fig. 2 DET plot clean versus airport noise

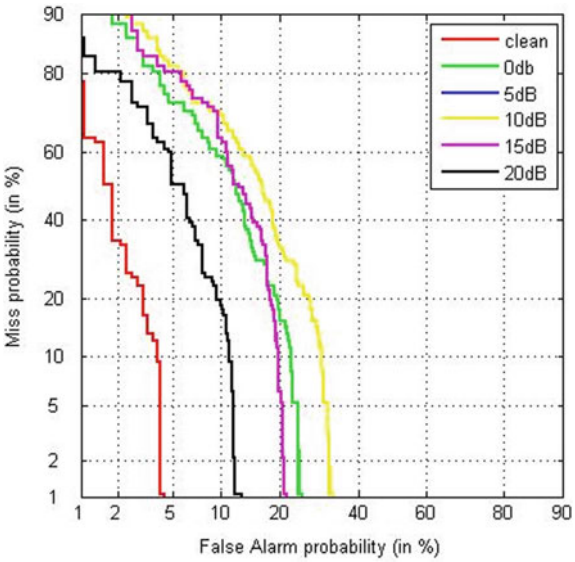

Fig. 3 DET plot of clean versus car noise

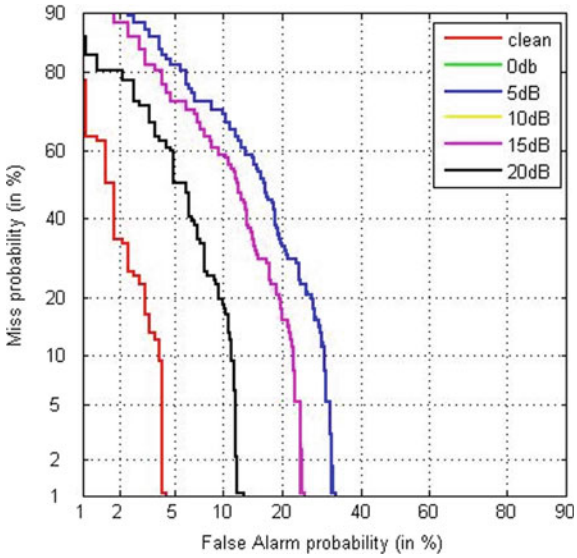

Fig. 4 DET plot clean versus street noise

represents the DET plot of clean versus car noise. In the above figure no separate visible curve line for 5 and 10 dB is noticed.

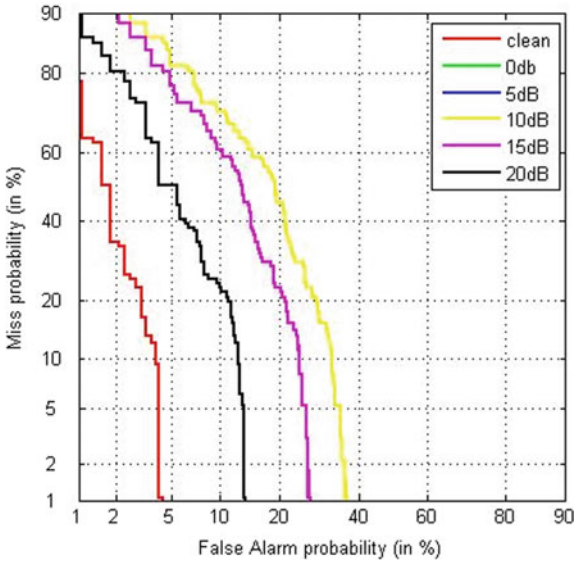

Fig. 5 DET plot of clean versus train noise

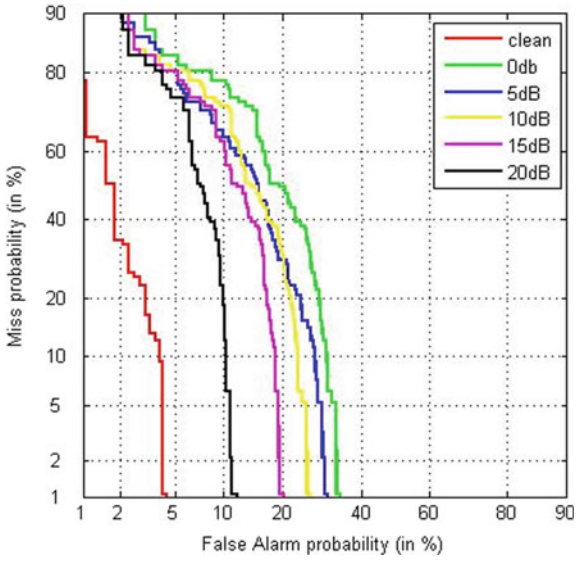

Fig. 6 DET plot clean versus exhibition noise

6 Conclusion

In the present work, an experiment has been performed using NIST 2003 and AURORA database for the impact of noise levels for SVM-GMM based speaker recognition system for various noisy environments. The recognition accuracy of SVM-GMM baseline system is seen to be increased to that of GMM based system

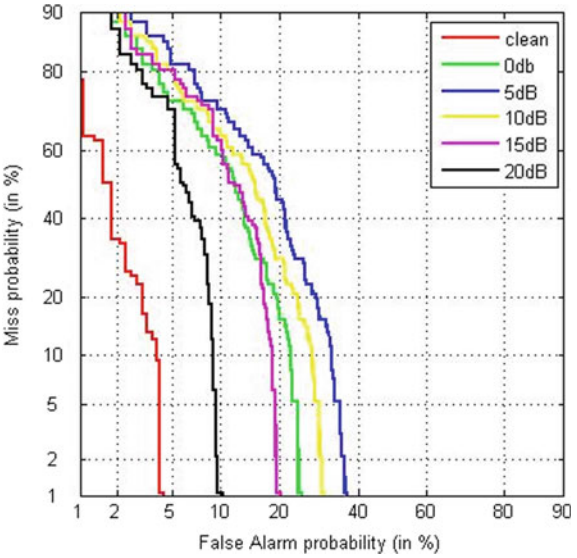

Fig. 7 DET plot of clean versus restaurant noise

for clean environment. From the results, it is also seen that recognition accuracy increases with an increase in SNR in the range of 5 dB to 20 dB for various noisy environments.

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Performance Evaluation of Normalization Techniques in Adverse Conditions

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Abstract

This paper explores the behavior of different normalization techniques viz. cepstral mean normalization, cepstral variance normalization, cepstral mean subtraction. cepstral mean and variance normalization, wiener filter, and spectral subtraction in noisy conditions. The performance parameters viz. EER (Equal Error Rate) and DCF (Detection Cost Function) has been calculated using NIST 2003 SRE and Aurora 2 with the help of various normalization techniques considered in this paper for different noisy backgrounds at 0, 5 and 10 dB signal-to-noise ratio. The experimental results obtained from these techniques reveal that cepstral mean normalization (CVN) normalization method is found to be better when compared to other normalization techniques used in this paper.

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Keywords: CMN; CVN; CMS; CMVN; SS; Wiener-Filtering, signal-to-noise ratio.

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1. Introduction- Voice biometric is one of the most prominent source of authentication in many areas like banking, online shopping, ATM transaction, access control, database security and applicable in many areas where it used for security purpose. Voice biometric system verifies the identity of a claimed person based on the extracted features of speech by comparing it with the stored voice templates. The performance of speaker recognition systems degrades in presence of noise [1 - 2]. Feature compensation (normalization) techniques are widely and effectively used for speaker recognition task such as speaker verification and speaker identification. Normalization process reduces the effect of noise and alleviates linear and non-linear channel effects. Robustness issue of the system can be improved by applying the normalization techniques [3].

To improve the performance of speaker recognition system various normalization techniques have been proposed which compensate the effects of environmental mismatch [4 – 9]. Robustness issue of speaker verification system has been improved by applying normalization techniques. Chougule and Chavan [4] have used CMN technique to minimize the influence of convolution noise in Hindi language based speech database. Barras and Gouvam [5] have presented some experimental analysis on text independent cellular data with the help of CMS, T-norm, Z-norm normalization techniques. Al-Kaltakchi et. al [6] have studied the speaker identification system which uses PNCCs and MFCC for feature extraction and CMVN as well as FW for the normalization of the system on acoustic model. Grozdic et. al [7] used various normalization techniques such as CVN, CMN, CMVN, CGN in their analysis of whisperd speech recognition system. Hardt and Fellbaum [8] used the spectral subtraction technique for analyzing telephonic based text dependent speaker verification system using different noises. Upadhyay and Jaiswal [9] have carried out the enhancement of single channel speech in stationary environments with the help of Wienner filtering normalization technique.

In this study, various normalization techniques have been considered for different noisy conditions. For the analysis NIST 2003 SRE and Aurora 2 data has been used for the calculation of performance parameters.

2. Normalization techniques

Normalization techniques are implemented to lower the noise impact, speech signal distortion and channel distortion. In paper, we discuss some normalization strategies, which are as follows:

2.1 Cepstral mean normalization (CMN)

CMN is the one of the simplest feature normalization technique to execute and it gives numbers of the advantages compared to advanced algorithms. To obtain normalized vector $\hat{x}_t$ CMN subtracts the mean feature vector μ_x from each vector x_t [10].

$$\mu_x = \frac{1}{T}\sum_t x_t \tag{1}$$

$$\hat{x}_t = x_t - \mu_x \tag{2}$$

2.2 Cepstral variance normalization (CVN)

Cepstral variance normalization (CVN) is a supplement technique of cepstral mean normalization which estimates varianceσ_n, of each cepstral dimension and normalizes it to unity [7].

$$C_{n,t}^{CVN} = \frac{C_{n,t}}{\sigma_n} = \frac{C_{n,t}}{\sqrt{\frac{1}{T}\sum_{t=1}^{T}(C_{n,t}-\mu)}} \tag{3}$$

where n & t represents the nth cepstral dimension and the index of cepstral samples in the window respectively.

2.3 Cepstral mean subtraction (CMS)

Cepstral mean subtraction is one of the most extensively used normalization methods [11]. Reynolds [12] has reported an utterance X=$\{x_i\}$, i$\in[1, N]$ feature with a feature frame $\{x_i\}$, the mean vector (m) of all the frames for the given utterance, is considered as:

$$\mathrm{m} = \frac{1}{N} \sum_{i=1}^{N} x_i \tag{4}$$

The normalized feature $\hat{x}_t$ with CMS is expressed by

$$\hat{x}_t = x_i - m \tag{5}$$

2.4 Cepstral mean and variance normalization (CMVN)

Cepstral mean and variance normalization normalize both mean and variance algorithm.

$$\sigma x^2 = \frac{1}{T} \sum_{t=0}^{T-1} x_t^2 - \mu_x^2 \tag{6}$$

$$x_t = \frac{x_t - \mu_x}{\sigma_x}$$

After normalization, the mean of the cepstral sequence is zero, and it has a variance of one [13].

2.5 Wiener-filtering

The wiener filtering is wavelet-based used to suppress additive noise based on the concept of wiener gains which can be calculated given as,

$$k_m = \frac{S(a^2)m}{S(a^2)m + D(a^2)m} \tag{7}$$

where, $S(a^2)m$ and $D(a^2)m$ represents the speech power and noise power respectively [14].

2.6 Spectral subtraction (SS)

Boll in 1979 introduced spectral subtraction technique of speech enhancement which is used to reduce the additive noise [15-16].

$$y(m) = x(m) + n(m) \tag{8}$$

$y(m)$ represents noisy signal, $x(m)$ is the speech signal and $n(m)$ is the noise.
In frequency domain it can be represents as follow:

$$Y(j\omega) = X(j\omega) + N(j\omega) \tag{9}$$

where, $Y(j\omega), X(j\omega), N(j\omega)$ is fourier transforms of $y(m), x(m), n(m)$, respectively.

3. Baseline System based on GMM-UBM

Fig.1 shows the basic structure of ASR system, which consists following phases: pre-processing, front-end processing/feature extraction, training of model and testing/recognition.

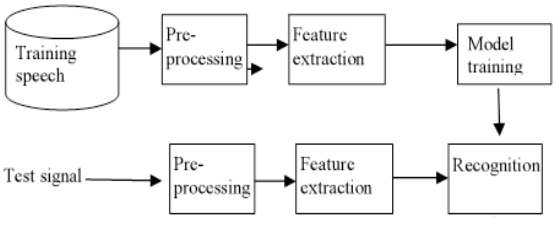


Fig. 1 Basic framework structure of ASR system [17]

3.1 Pre-processing

In pre-processing process speech data has been prepared. Pre-processing includes various tasks like sampling, pre-emphasis, framing (segmenting the speech into frames) and windowing.

3.2 Front end processing / feature extraction

Mel frequency cepstral coefficients, Bark scale filter bank cepstrum coefficients, Linear prediction cepstral coefficients and Perceptual linear prediction cepstral coefficients are the most common used acoustic vectors for speaker verification. All the features based on the spectral information are derived from a short time- windowed segment of speech. MFCC features are derived from the FFT power spectrum whereas LPCC and PLPC use an all-pole model to represent the smoothed spectrum. The proposed normalization technique used Mel-Frequency Cepstral Coefficients (MFCC) feature extraction for further processing [18].

3.3 Training of speaker model

GMM-UBM methodology has been considered as a speaker model for testing the speaker verification system; Fig. 2 shows the GMM-UBM based framework of speaker verification system. Firstly, speech features are extracted using mel-frequency cepstral coefficients after that a gender dependent universal background model is generated which based on Expectation Maximization (EM) algorithm.

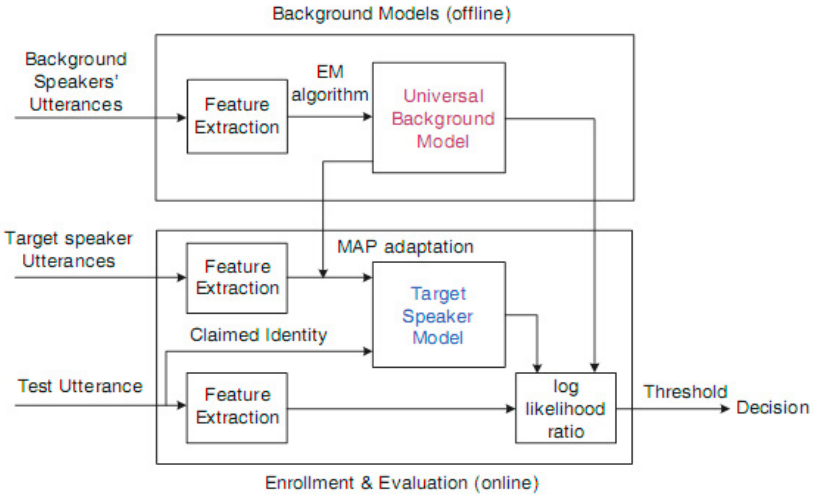


Fig. 2 GMM-UBM framework for speaker verification [19]

The computation of log-likelihood ratio $\wedge\ (X)$ has been done by scoring the test feature vectors against the claimant model and the universal background model by the expression given below:

$$\wedge\,(X) = \log p\left(X|\lambda_{hyp}\right) - \log p\left(X|\lambda_{\overline{hyp}}\right)$$

The claimant speaker is accepted if the value of $\wedge\,(X) \geq \theta$ or otherwise rejected. The substantial concern in speaker verification is to obtain a decision threshold θ for the decision making [20].

4. Experiments and results

In the present work, system performances are analysed in various types of additive noise background such as airport noise, babble noise, car noise and train noise at 0, 5, and 10 dB signal-to-noise ratio (SNR).

4.1 Database

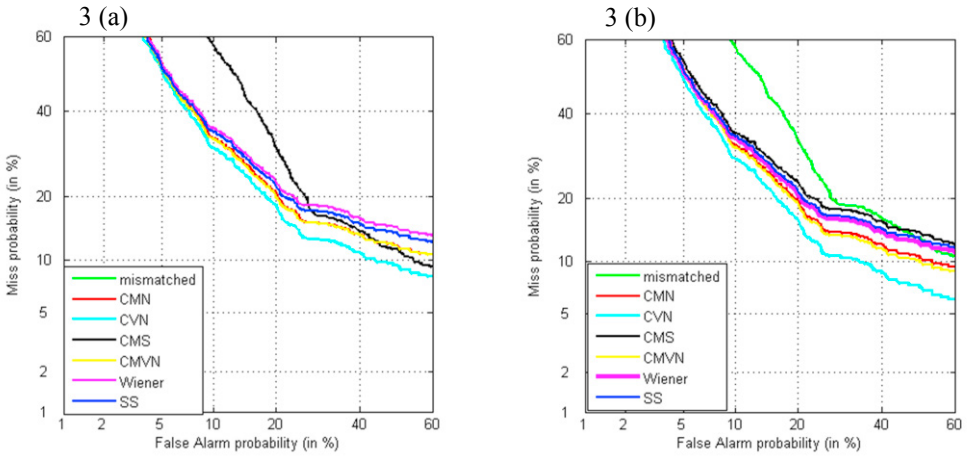
NIST -2003 –SRE database is used for the system development. The database consists of conversational speech of 149 male speakers. Aurora 2 database has been used for artificially simulating noisy environments at different SNR level.

4.2 Performance evaluation

In the present study, equal error rate (EER) has been used to quantify the performance of the system. Detection Error Trade-off (DET) curve is obtained by plotting the 'miss probability' (when a true identity is rejected) false alarm' (when an imposter's claim is accepted). The EER is the operating point in the DET curve where both the miss rates (P_{miss}) and false (P_{fa}) rates become equal, whereas DCF is the base estimation of a weighted cost function which is given by $0.01 * P_{miss} + 0.99 * P_{fa}$.

4.3 Results and discussions

Figures 3 - 5 represent the DET plots of mismatched conditions. The various normalization techniques which have been used in the paper are discussed in the section 2. Each set of curve in a subfigure deviate to a particular type of normalization methods in different noisy environments (airport noise, babble noise, car noise and street noise) at 0 dB, 5 dB and 10 dB SNRs respectively. The DET curve is consistently shifted towards origin with an increase in signal-to-noise ratio inferring performance improvement with reducing the strength of noise.. The performance summary of the normalization techniques is shown in Table 1. The order of precedence in terms of EER value for the system performance accuracy are mismatched, CMN, CVN, CMS, CMVN, Wiener filter and SS. MinDCF follows the same pattern with the exception of the way that they don't show a consistently pattern over the different techniques . The main exemption to this order is found in all noise types except babble noise at at 0 dB and 5 dB signal-to-noise ratios.



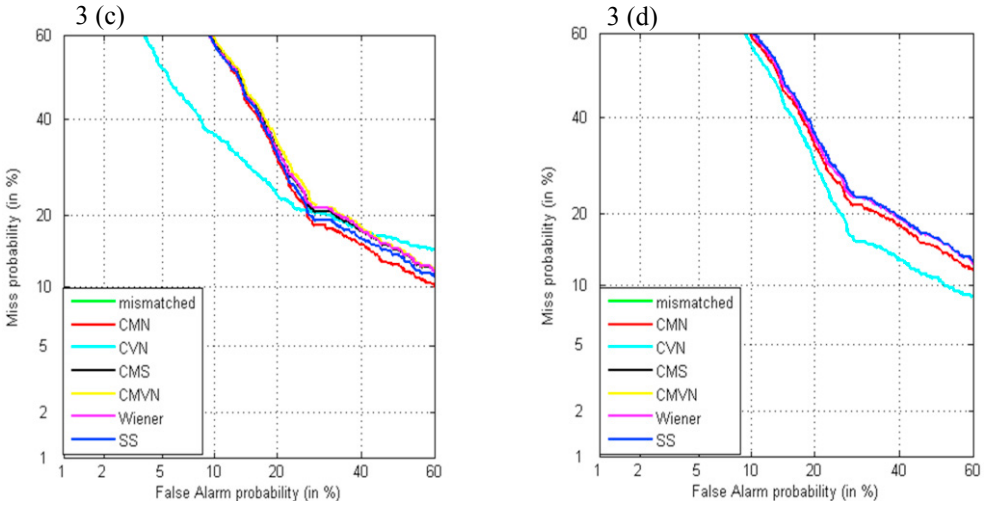
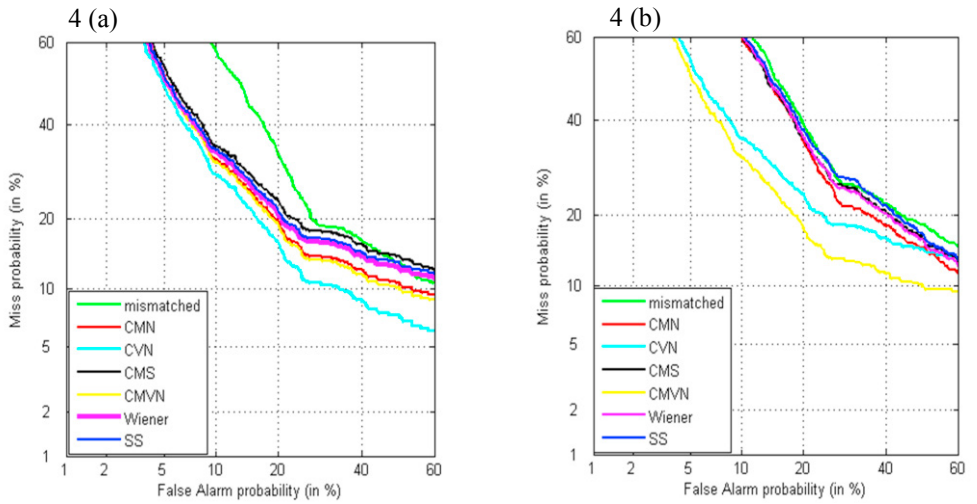


Fig. 3 DET plots of normalization techniques for (a) airport noise (b) babble noise (c) car noise (d) street noise at 0dB SNR



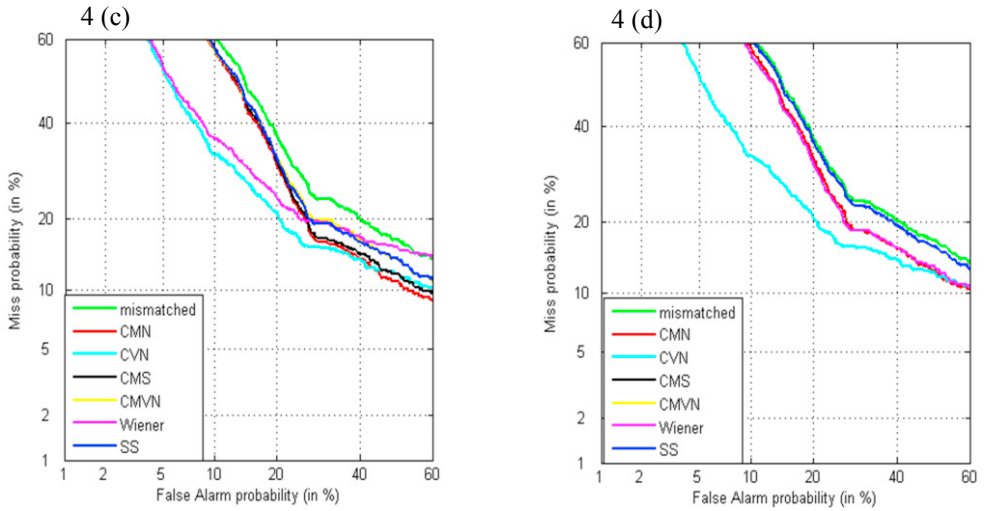
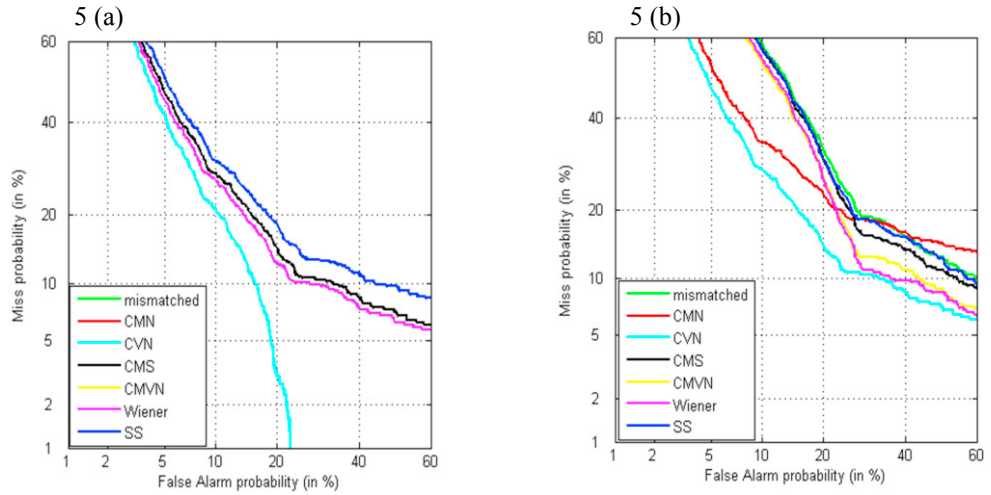


Fig. 4 DET plots of normalization techniques for (a) airport noise (b) babble noise (c) car noise (d) street noise at 5 dB SNR



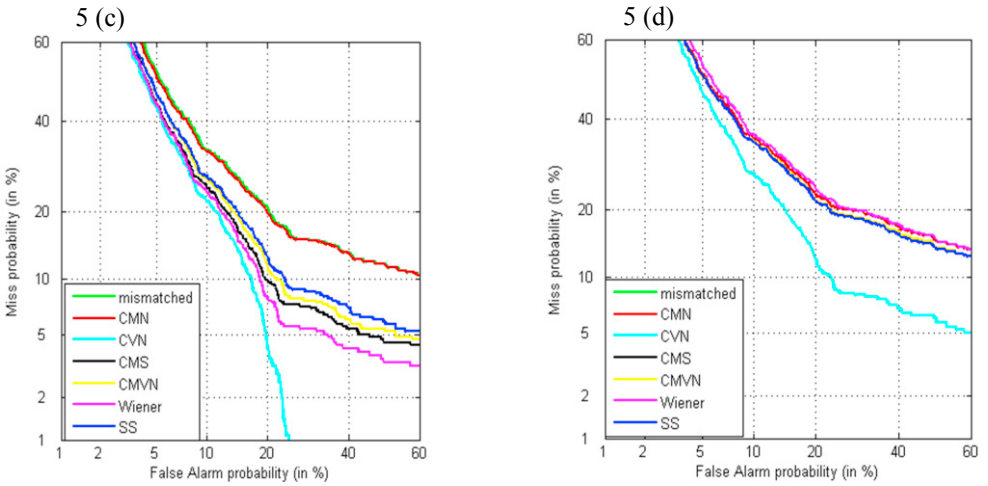


Fig. 5 DET plots of normalization techniques for (a) airport noise (b) babble noise (c) car noise (d) street noise at 10 dB SNR

Table 1 Performance of normalization techniques in different environments

SNR(dB)	Techniques	Airport		Babble		Car		Street	
		EER (%)	MinDCF	EER (%)	MinDCF	EER (%)	MinDCF	EER (%)	MinDCF
0	Mismatch	23.243	0.4204	28.4685	0.5393	25.5856	0.4683	26.3063	0.4853
	CMN	20.180	0.3733	26.8468	0.5015	24.1441	0.4384	25.5856	0.4709
	CVN	19.099	0.3481	23.9640	0.4330	22.7027	0.4238	23.0631	0.4114
	CMS	23.243	0.4204	27.0270	0.5128	24.8649	0.4552	26.3063	0.4114
	CMVN	19.819	0.3698	28.4685	0.5393	25.5856	0.4683	26.3063	0.4853
	WF	21.081	0.3986	27.7477	0.5250	25.0450	0.4590	25.9459	0.4793
	SS	20.721	0.3896	27.3874	0.5190	24.3243	0.4469	26.3063	0.4853
5	Mismatch	24.324	0.4430	27.0270	0.5123	26.4865	0.4899	26.6667	0.4943
	CMN	19.819	0.3607	25.7658	0.4709	23.2432	0.4186	24.3243	0.4420
	CVN	17.838	0.3265	21.2613	0.4022	20.3604	0.3751	20.1802	0.3776
	CMS	21.261	0.3986	26.3063	0.4967	23.4234	0.4240	26.3063	0.4114
	CMVN	19.279	0.3553	19.0991	0.3481	24.5045	0.4469	26.3063	0.4114
	WF	20.180	0.3776	26.3063	0.4962	21.9820	0.4112	23.9640	0.4354
	SS	20.540	0.3842	27.3874	0.5190	24.5045	0.4469	26.3063	0.4853
10	Mismatch	19.279	0.3553	24.3243	0.4424	20.1802	0.3733	22.1622	0.4145
	CMN	14.054	0.2131	20.9009	0.3981	19.8198	0.3688	21.9820	0.4054
	CVN	13.874	0.2093	17.2973	0.3166	14.2342	0.2196	16.7568	0.2943
	CMS	17.477	0.3177	22.8829	0.4132	15.3153	0.2738	20.7207	0.3902
	CMVN	13.874	0.2111	21.9820	0.3759	16.3964	0.2896	21.0811	0.3946
	WF	16.577	0.3008	21.8018	0.3664	14.9550	0.2562	19.8198	0.3632
	SS	14.414	0.2209	23.6036	0.4295	16.9369	0.2997	20.9009	0.3928

Table 2 Performance summary of normalization techniques in different environments

Techniques	EER (%)
Mismatch	24.504
CMN	22.222
CVN	19.219
CMS	23.511
CMVN	21.891
WF	22.312
SS	22.778

The worst case scenario shown by mismatched condition for all types of noisy environment with an average value of EER equals 24.504% over all the noises considered for various SNRs. The MinDCF values varied in the range of 0.2111-0.4853 (Table 1). CMN normalization method shows decrement of 2.282% EER over the mismatch condition. However CVN performs far better than other utilized techniques with an improvement of 5.285% EER for airport, babble, car and street background environments shown in Table 2 with respected to mismatched condition. CMS shows minor improvement of 0.993% decrement of EER over the mismatch condition. Other used methods such as CMVN, Wiener filter and SS shows 2.613, 2.192 and 1.726% respectively decrement in EER with respect to mismatch condition. Wiener filter is seen moderately better than CMN, CMVN and SS normalization methods. Compared to other methods CVN show the highest 7.928% drop in EER in case of babble noise at 5 dB SNR, while reduction of 7.027% in EER for babble noise at 10dB SNR has been noticed.

The comparative improvement of normalization methods performance is visible. The average value for EER of 22.222% for CMN, 19.219% for CVN, 23.511% for CMS, 21.891% for CMVN, 22.312% for wiener filter and 22.778% for SS across all noisy environments is acheived.

5. Conclusions

Normalization techniques have been used to compensate the effects of environmental mismatch. In this study behavior of normalization techniques viz. cepstral mean normalization, cepstral variance normalization, cepstral mean subtraction, cepstral mean and variance normalization, wiener filter and spectral subtraction have been studied under different noisy environments such as airport noise, babble noise, car noise and street noise at 0,5 and 10 dB signal-to-noise ratio. On the basis of experimental results it has been concluded that the cepstral variance normalization (CVN) method is comparatively better as compared to other used normalization methods which have been used in this paper and it reveals 5.285% of EER improvement over mismatch condition across all noisy environments and all SNRs whereas other used methods show improvement of 2.282% for CMN, 0.993% for CMS, 2.613% for CMVN, 2.192% for wiener filter and 1.726% for SS respectively over mismatch condition across all SNRs with respect to mismatch condition.

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Performance of Speaker Recognition System Using Kernel Functions Approach for Different Noise Levels

Renu Singh, Arvind Kumar Singh, and Utpal Bhattacharjee

Abstract Speaker recognition is one of the most popular voices biometric technique used for security reason in many areas like banking system, online-shopping, database access etc. The recognition performance of speaker recognition system is very satisfactory in noise-free environments, whereas the improved performance in case of low level signal-to-noise ratio (SNR) is the need in the present days. Hence, in this study speaker recognition performance has been evaluated at different signal-to-noise ratios using SVM-based various kernel functions approach and principal component analysis (PCA). The proposed scheme has been applied on NIST 2003 and AURORA dataset and found that the recognition accuracy and running time improves at low level SNRs using kernel functions.

Keywords Speaker recognition system · SVM · Principle component analysis (PCA) · Signal-to-noise ratio

1 Introduction

Speaker recognition is a method of recognizing a speaker's voice by utilizing explicit information comprised in speech waves [1, 2].This methodology can be used to substantiate the characteristics claimed by the person who wants to access the systems i.e. enabling the access control of different services with the help of voice. The various applications of speaker recognition system are voice dialing, phone banking, shopping over phone, database access services, reservation services, services on voice mail

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and controlling security aspects for secret data and remote access of PCs. Another significant use of speaker recognition technology is its utilization for criminological purposes [3]. Generally, the speaker recognition by a machine comprises feature extraction, speaker modeling or training and testing [4]. The estimation of the speaker specific features from the speech signal is done using feature extraction. Thereafter, the speaker model is trained with the use of these features. Finally, in the stage of testing, recognition of speaker is performed by matching with the pattern.

Support vector machine (SVM) is one of the highly used classification technique in analyzing the performance of speaker recognition [5–7]. The support vector machine provides a natural solution for binary class problems. It is one of the popular learning techniques for solving regression and classification problems. SVM has been applied in various areas viz. face, text, 3D object, speech, speaker recognition systems. SVM uses different kernel functions such as linear, nonlinear, polynomial, radial basis, sigmoid, Gaussian, cubic and quadratic etc. Astuti and Adiwijaya have carried out SVM with principal component analysis (PCA) for the classification of microarray data [8]. Bassma have used SVM for the improvement of vehicle localization in urban canyons [9]. Zhao et al. [10] have used nonlinear kernel nuisance attribute projection for speaker verification using NIST SRE data. Kernel PCA feature extraction along with support vector machine classification are effectively used for through-wall human being detection [11]. Das et al. have used linear polynomial and radial basis function kernels for the analysis of gene data set [12].

The focus of this work is to investigate the accuracy of the speaker recognition system in different noise levels using different kernel functions viz. linear, quadratic, cubic and Gaussian.

2 Speech Data Classification

The various steps in this analysis consist of pre-processing/feature extraction, classification and performance evaluation as shown in Fig. 1. In the feature extraction step, principal component analysis (PCA) has been used for dimension reduction which uses mapping function. The different processes which are used in this extraction are data centering, covariance matrix calculation, Eigen value and Eigen vector calculation. In classification, SVM helps in modeling the complex data set and separate different classes and maximize the margin. SVM uses a nonlinear mapping approach for converting the original data to a high dimension and helps in linear separation of data creating a hyperplane (decision boundary). The performance evaluation is executed in the final step.

In this work, two different types of experiments are performed. Initially the experiment is performed to analyze the effectiveness of number of components considered in PCA. The various experiments are carried out on NIST 2003 SRE clean data set to visualize the effect on the accuracy of various Kernel functions. The second experiment in the proposed method is performed to visualize the recognition accuracies as well as running time. The experiments are conducted on noisy data namely: 0, 5,

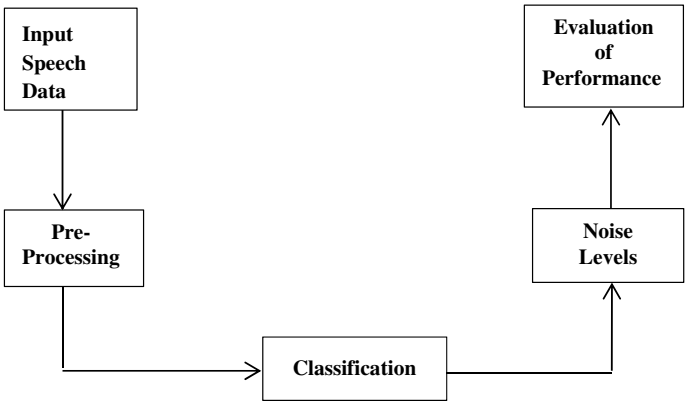

Fig. 1 Performance evaluation steps

10, 15 and 20 dB signal-to-noise ratio. The total numbers of 12 scenarios of experiment were considered for each data set, as shown in Table 1. The general classifier characteristics for Kernel function operation has been given in Table 2.

Table 1 Experiment scenarios [8]

Scenario	Dimension reduction	SVM Kernels
1.	None	Linear
2.	None	Quadratic
3.	None	Cubic
4.	None	Fine Gaussian
5.	None	Medium Gaussian
6.	None	Coarse Gaussian
7.	PCA	Linear
8.	PCA	Quadratic
9.	PCA	Cubic
10.	PCA	Fine Gaussian
11.	PCA	Medium Gaussian
12.	PCA	Coarse Gaussian

Table 2 General classifier characteristics

Kernel function	Linear, quadratic, cubic, Gaussian
Kernel scale	Automatic
Box constraint level	1
Multiclass method	One-vs-One
Standardize data	True

3 Kernel Functions and Expressions

The various kernel functions used in the SVM classifier are linear, quadratic, cubic and Gaussian functions. The expressions of these kernel functions are expressed as follows [9];

Linear function:

$$k(x_i, x_j) = x_i^T x_j + c \tag{1}$$

Quadratic function:

$$k(x_i, x_j) = 1 - \frac{\|x_i - x_j\|^n}{\|x_i - x_j\|^n + c} \tag{2}$$

Cubic function:

$$k(x_i, x_j) = \left(x_i^T x_j + 1\right)^n \tag{3}$$

Gaussian function:

$$k(x_i, x_j) = \exp\left(-\frac{\|x_i - x_j\|^n}{2\sigma^2}\right) \tag{4}$$

where x_i and x_j are input space vectors, n is order of the kernel and c is a constant.

4 Results and Analysis

The effect of kernel function approach for the clean speech data and noisy data at different SNR has been studied in this paper. For the effective analysis, various scenarios with and without PCA are considered for clean speech data which can be seen in Table 3. It is clearly seen that accuracy percentage of scenario using PCA is found to be improved except linear case, whereas there are no changes in accuracy percentages for fine and coarse Gaussians. The comparison of accuracy for with and

Table 3 Accuracy (%) of SVM Kernel function in various scenarios

Case	Linear	Quadratic	Cubic	Fine Gaussian	Medium Gaussian	Coarse Gaussian
Without PCA	95	85	85	85	85	100
With PCA	90	90	90	85	100	100

without PCA are done at number of components after PCA equals 1 and variance kept after PCA equals 95%.

Here, total 9 numbers of experimental scenarios are considered for the calculation of the accuracies of 6 SVM Kernel functions. The various scenarios for different variance thresholds which are 36.5, 48.44, 66, 80.14, 90.34, 95.08, 97.52, 98.85 and 100% are considered as per Astuti and Adiwijaya [9]. To check the Kernel functions accuracy the first scenario chooses a minimum number of components and the corresponding value of the variance $\geq$36.5%, and so on. The results are calculated for 6 numbers of SVMs. The accuracies for various numbers of components and variance for different scenarios are presented in Table 4.

The experimental results for noisy speech data using various scenarios and SNRs are shown in Table 5. The accuracies with PCA are found to be increased for linear,

Table 4 Accuracyfor PCA parameters for clean speech data

Components after PCA	1	2	4	8	16	25	34	39	39
Variance kept after PCA(%)	36.5	48.44	66	80.14	90.34	95.08	97.52	98.85	100
Accuracy (%)									
Linear	75	80	85	90	75	75	95	75	75
Quadratic	75	85	90	85	80	90	90	85	90
Cubic	70	85	90	90	80	95	85	85	90
Fine Gaussian	65	80	85	75	75	75	85	75	75
Medium Gaussian	75	80	95	90	75	75	75	75	75
Coarse Gaussian	75	75	75	75	75	75	75	75	75
Average	72.5	80.8	86.6	84.2	76.66	80.83	84.16	78.33	80

Table 5 Accuracyfor proposed methods for noisy speech data

Scenario	Accuracy (%)				
	0 dB	5 dB	10 dB	15 dB	20 dB
1.	60	70	75	85	95
2.	65	70	85	90	90
3.	60	70	85	90	90
4.	60	65	60	85	85
5.	65	65	65	85	85
6.	60	65	60	85	95
7.	70	75	75	85	90
8.	75	75	80	85	85
9.	70	85	80	90	85
10.	60	65	60	85	85
11.	65	65	60	85	95
12.	60	65	60	85	95

Table 6 Training time for proposed methods

Scenario	0 dB	5 dB	10 dB	15 dB	20 dB
1.	0.5883	1.0826	1.0440	1.1933	1.1467
2.	0.5903	1.0258	1.0317	1.2308	1.0862
3.	0.6298	1.0316	1.0216	1.0771	1.0594
4.	0.7259	1.0421	1.1473	1.0756	1.0530
5.	0.5891	1.0299	1.0804	1.1434	1.0081
6.	0.6342	1.1789	1.0507	1.0156	1.1173
7.	0.5663	0.5293	0.5312	0.5538	0.6021
8.	0.5876	0.5774	0.6192	0.7662	0.6056
9.	0.5881	0.5767	0.5321	0.5983	0.5410
10.	0.5815	0.5412	0.6226	0.7907	0.6189
11.	0.5887	0.5477	0.5414	0.6390	0.5456
12.	0.6125	0.5477	0.5508	0.5913	0.5497

quadratic and cubic Kernels at 0 and 5 dB SNRs. However, it remains same for all the Gaussian Kernels. It is also seen that the accuracies do not improve for higher SNRs in the range of 10–20 dB. The running times for all the scenarios for different SNRs are depicted in Table 6. It is seen that PCA greatly reduces the running time for all the SNRs considered.

5 Conclusion

In the present work, experiments have been performed using NIST 2003 and AURORA database for the analysis of Kernel functions at various scenarios for different SNRs. The accuracy and running time of SVM using Kernel approach and PCA are found to be improved for low level SNRs. The quadratic Kernel function is found to be better at 0 dB, whereas Cubic Kernel function is found to be better at 5 dB SNR.

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An Analysis of Phase-Based Speech Features for Tonal Speech Recognition

Jyoti Mannala, Bomken Kamdak, and Utpal Bhattacharjee

Abstract Automatic speech recognition (ASR) technologies and systems have made remarkable progress in the last decade. Now-a-days ASR based systems have been successfully integrated in many commercial applications and they are giving highly satisfactory results. However, speech recognition technologies as well as the systems are still highly dependent on the language family for which it is developed and optimized. The language dependency is a major hurdle in the development of universal speech recognition system that can operate at any language conditions. The language dependencies basically come from the parameterization of the speech signal itself. Tonal languages are different category of language where the pitch information distinguishes one morpheme from the others. However, most of the feature extraction techniques for ASR are optimized for English language where tone related information is completely suppressed. In this paper we have investigated short-time phase-based Modified Group Delay (MGD) features for parameterization of the speech signal for recognition of the tonal vowels. The tonal vowels comprises of two categories of vowels—vowels without any lexical tone and vowels with lexical tone. Therefore, a feature vector which can recognize the tonal vowels can be considered as a speech parameterization technique for both tonal as well as non-tonal language recognizer.

Keywords Feature analysis · MGD feature · Phase-based features · Speech recognition · Tonal language

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1 Introduction

Natural languages are broadly classified into two categories—tonal and non-tonal based on their dependency on lexical tone. In tonal language, the lexical tone plays an important role in distinguishing the syllables otherwise similar whereas in non-tonal language the lexical tone has no significant role in distinguishing the syllables. English, Hindi, Assamese are the example of non-tonal language whereas Chinese, Japanese, language of South East Asia, Sweden, Norway and Sub-Sahara Africa are tonal languages [1]. Modern speech recognition research has a half century long legacy. The technology and the systems developed speech recognition have already registered significant progress and many systems are already commercialized. However, those systems are optimized with non-tonal languages, particularly for English language. As a result, when these systems are used for tonal speech recognition their performance degrades considerably. Since the large sections of the world population are speaker of tonal language, for the global acceptability of the speech recognition technology and system, it must be efficient in recognizing in tonal as well as non-tonal language.

One of the major reasons for the system developed for non-tonal language fail to deliver consistent performance in tonal language is due to the non-consideration of the lexical tone related information. Lexical tones are produced as a result of excursion of the fundamental frequency and these informations are discarded in non-tonal speech recognition system as a measure of performance optimization and due to robustness issues as it contains very little useful information for non-tonal speech recognition system.

In the recent years many attempts have been made for developing tonal speech recognition system [2–4]. Such systems are developed considering the fact that a tonal syllable has two components—phonetic and tone. The phonetic component gives information about the base phonetic unit which is similar with non-tonal speech and a tonal unit which gives information about the tone associated with that phonetic unit. As a result, the tonal speech recognition system relies on two sets of features—Spectral features like MFCC for base phonetic unit recognition and prosodic features for associated lexical tone recognition. The scores obtained from both are combined together to arrive at a decision on underlying syllabic unit. However, the prosodic features are highly sensitive to ambient conditions. As a result, the tonal speech recognition systems based on prosodic features are highly susceptible to ambient conditions.

The speech recognition system relies on short-term spectral property of the speech signal in order to exploit the short-term stationary property of the speech signal. To extract the short-term property, Short Term Fourier Transform (STFT) is used. STFT returns the short-term magnitude and phase spectral of the speech signal. However, in most of the cases magnitude spectra is retain to extract spectral features like Mel Frequency Cepstral Coefficient (MFCC) and phase spectral is completely discarded due to the practical difficulty in phase wrapping [5, 6]. However, the recent research has established the importance of phase spectra in speech processing

applications like speech recognition, speaker recognition, emotion recognition and speech enhancement [7].

In this paper we have analyzed the tonal phoneme discrimination capability of phase-based features. The performances of phase-based features have been evaluated for tonal phoneme discrimination.

2 Feature Vector for the Representation of Tonal Phonemes

The Fourier transform of a discrete time speech signal $x(n)$ is given by.

$$X(\omega) = |X(\omega)|e^{j\phi(\omega)} \tag{1}$$

where $|X(\omega)|$ is the magnitude spectra and $\phi(\omega)$ is the phase spectra of the speech signal. There are number of speech processing difficulties in using the phase spectra directly in Automatic Speech Recognition (ASR). Two most critical problems are—firstly a phase spectrum is highly sensitive to the exact positioning of the short-time analysis window. It has been observed that for a small shift in analysis window, the phase spectrum changes dramatically [8]. Secondly, the phase spectrum values are only computable within the range $\pm\pi$, called principal phase spectrum. The value changes abruptly due to the wrapping effect beyond this range. However, for better representation of the phase spectra for automatic speech recognition, the spectra must be unwrapped. The major problem with this unwrapping is that any multiple of 2π is added to the phase spectra without changing the value of $X(\omega)$. Recent studies have shown that phase spectrum can be used for speech applications and gives promising results [9, 10]. Among the phase based features extraction techniques, Group Delay Function (GDF) and All-pole Group Delay Function (APGD) are widely used. In the present study we have used a modified version of GDF called Modified Group Delay (MGD) function for extracting the phase based features due to their promising performance in speech recognition [11].

The Group Delay Function is derived by taking the negative derivation of the Fourier phase spectrum $\phi(\omega)$, written as [12, 13]:

$$\begin{aligned}\tau(\omega) &= -\frac{d(\phi(\omega))}{d(\omega)} \\ &= \frac{X_R(\omega)Y_R(\omega) + X_I(\omega)Y_I(\omega)}{|X(\omega)|^2}\end{aligned} \tag{2}$$

the angular frequency ω is limited to $(0,2\pi)$, $Y(\omega)$ is the magnitude of the Fourier transform of the time-weighted version of the speech signal given by $y(n) = nx(n)$. The subscript R and I denotes the real and imaginary parts of the signals. The features derived from GDF often leads to an erroneous representation near the point of discontinuity. It is due to the denominator $|X(\omega)|^2$ which tends to 0 near the point of

discontinuities. Therefore, the group delay function is modified, which is given as [14]

$$\tau(\omega) = \frac{\tau_p(\omega)}{\left|\tau_p(\omega)\right|}\left|\tau_p(\omega)\right|^{\alpha} \tag{3}$$

where

$$\tau_p(\omega) = \frac{X_R(\omega)Y_R(\omega) + X_I(\omega)Y_I(\omega)}{|S(\omega)|^{2\gamma}} \tag{4}$$

where $S(\omega)$ is the cepstrally smoothed form of $|X(\omega)|$. α and γ controls the range dynamics of the modified group delay function. Here,

$$P(\omega) = X_R(\omega)Y_R(\omega) + X_I(\omega)Y_I(\omega) \tag{5}$$

is called the product spectra of the speech signal which includes both magnitude and phase information [15].

3 Speech Database

In the present study, we have created a speech database of Apatani Language of Arunachal Pradesh of North East India to analyze the performance of phase-based features for tonal speech recognition in mismatched environmental conditions. The Apatani language belongs to the Tani group of language. Tani languages constitute a distinct subgroup within Tibeto-Burman group of languages [16]. The Tani languages are found basically in the contiguous areas of Arunachal Pradesh. A small number of Tani speakers are found in the contiguous area of Tibet and only the speakers of Missing language are found in Assam [17]. The Apatani language has 06(six) vowels and 17 (seventeen) consonants [18]. To record the database, 24 phonetically rich isolated tonal words have been selected. The words are spoken by 20 different speakers (13 males and 7 females). The recording has been done in a controlled acoustical environment at 16 kHz sampling frequency and 16 bit mono format. A headphone microphone has been used for recoding the database. The words are selected in such a way that each tonal instance of the vowel has at least 5 instances among the words. Since the tone associated with the vowel is sufficient to identify the tone associated with the entire syllable [3, 19], therefore, in the present study we have evaluated the phone discrimination capability and robustness issue of the phase-based features with reference to their tonal vowel discrimination capability. Each tonal instance of a vowel has been considered as different tonal vowel. For example, the vowel [a:] have three associated tones—rising, falling and level. Thus vowel [a:] gives raise to the tonal vowels [á:] ([a:] rising), [à:] ([a:] falling) and [ā:] (([a :] level). Considering the tonal instances as a separate vowel, we get sixteen

Table 1 Apatani vowels and their tonal instances

Vowel	Tonal instances		
	Rising	Level	Falling
ɪ	[ɪ́]	[$\overline{\text{ɪ}}$]	[ɪ̀]
ʊ	[ʊ́]	[$\overline{\text{ʊ}}$]	[ʊ̀]
ɑː	[ɑ́ː]	[$\overline{\text{ɑ}}$ː]	[ɑ̀ː]
ɛ	[ɛ́]	[$\overline{\text{ɛ}}$]	[ɛ̀]
ɔ	[ɔ́]	[$\overline{\text{ɔ}}$]	[ɔ̀]
ə	-	[$\overline{\text{ə}}$]	-

tonal vowels in Apatani language. The vowels and their tonal instances are given in Table 1. Since the vowel [ə] has only one tone, it is not taken into consideration while evaluating the performance of the feature vectors.

All the experiments are carried out using this database. The vowels are segmented from the isolated words for all its tonal instances. The segmentation has been done using PRAAT software which is followed by subjective verification.

4 Experiment and Results

To evaluate the performance of the features for tonal phoneme discrimination capability, both statistical methods and Hidden Markov Model based recognizer have been used.

Euclidean distances between the feature values extracted from each pair of tonal phoneme have been computed. The Euclidean distance gives an indication of the linear separation among the tonal vowels with reference to phase-based features. Higher the value of Euclidean distance indicates better discrimination capability for the feature vector.

Fisher's Discrimination ration (F-ratio) [20] has been used as a quantitative measure for the tonal phoneme discrimination capability of the phonemes. F-ratio is defined as:

$$F = \frac{\text{Variance of the tonal phoneme mean}}{\text{Average intra} - \text{phoneme variance for all phonemes}}$$

The above ratio can be computed as:

$$F = \frac{\frac{1}{P}\sum_{i\in P}\sqrt{(\mu_i - \overline{\mu})^2}}{\frac{1}{P}\sum_{i\in P}\left(\frac{1}{T}\sum_{\beta\in T}\sqrt{\left(\left|x_\beta^{(i)} - \mu_{\beta,i}\right|^2\right)}\right)} \tag{7}$$

where $\overline{\mu}$ is the average mean for all the tonal phonemes, μ_i is the average mean for the base phoneme i, $\mu_{\beta,i}$ is the average mean for phoneme i for tone β, $x_\beta^{(i)}$ indicates an instance of the phoneme i for tone β. Higher the value of F-ratio indicates that the feature is capable of discriminating among the tonal phonemes.

To evaluate the performance of the phase-based feature set in recognizing the tonal phonemes, a Left-to-Right Hidden Markov Model (LRHMM) has been used. The LRHMM is suitable for speech recognition due to its capability to model the time varying property of the speech signal. The number of HMM states is determined experimentally. In the present model, 6 (six) states have been used. Each state is represented by a single Gaussian distribution function given by [21].

$$P\left(x|\mu,\sigma^2\right) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left(\frac{-(x-\mu)^2}{2\sigma^2}\right) \tag{8}$$

where x is the observation vector, μ is the Gaussian mean vector and σ^2 is the variance. The forward–backward algorithm has been used for training the HMM model. Clean speech signals have been used for training the models.

To extract the short-time MGD features the speech signal is first pre-emphasized with emphasizing factor 0.97 and then framed by a Hamming windows of 30 ms duration and 10 ms frame rate. The phase-based MGD features are extracted from the windowed speech signal using the method described in the Sect. 2.

In the first set of experiments we have evaluated the phoneme discrimination capability of the MGD features in the context of tonal vowel recognition. The feature values are computed from each instance of the tonal vowels. For each tonal vowel, the average value for each dimension of the feature vector has been computed ignoring the outliers. The Euclidean distances have been computed between each tonal vowel with all the other tonal vowels and their average has been taken. Table 2 gives the average Euclidean distances of each tonal vowel from all the other tonal vowels. Table 3 presents the average Euclidean distances among different categories of tonal vowels.

From the above experiments it has been observed that phase-based MGD features are suitable in discriminating the tonal vowels. They possess discrimination ability even when the base phoneme of the tonal vowels is same and distinction among them is due to underlying tone only or vice versa.

To assess the suitability of the MGD features for tonal vowel recognition, we have computed the F-ratio values for the features. Higher the value of F-ratio among different groups indicates better discrimination ability of the feature with respect to that grouping factor. In the present study we have evaluated the computed F-ratio

Table 2 Average euclidean distances of each tonal vowel from all the other vowels

Tonal Vowel	Average euclidean distance from the other tonal vowels	Tonal vowel	Average euclidean distance from the other tonal vowels	Tonal Vowel	Average euclidean distance from the other tonal vowels
[ɪ́]	0.7513	[ʊ̀]	0.9267	[ɛ̄]	1.2091
[ī]	0.7292	[ɑ́ː]	1.4317	[ɛ̀]	1.1002
[ɪ̀]	0.5993	[ɑ̄ː]	1.9577	[ɔ́]	1.6260
[ʊ́]	0.9437	[ɑ̀ː]	2.7468	[ɔ̄]	1.3167
[ʊ̄]	1.0653	[ɛ́]	1.1449	[ɔ̀]	2.0015

Table 3 Average Euclidean distance among different categories of tonal vowels

Average Euclidean distance among the vowels with same base phoneme but different tone	1.1496
Average Euclidean distance among the vowels with different base phoneme but same tone	0.9698
Average distance from the vowels with different base phoneme and tone	1.3589

value with grouping factors—same base-phoneme, same tone and different base phoneme and tone. The F-ratio values are listed in Table 4.

From the above experiments, it has been established that short-time phase based feature MGD has the capability to identify the tonal vowels even when they are distinct from each other only by tone or only by base-phoneme. This observation assets the fact that short-time phase based MGD feature is a better alternative than the combination of MFCC and Prosodic based features for tonal vowel recognition which have been evaluated in our earlier works [22].

In the next set of experiments, we have evaluated the performance of MGD feature for their tonal vowel recognition in terms of recognition accuracy of the HMM based recognizer. The model has been trained using clean speech database. 60% of the tonal

Table 4 F-ratio values under different grouping factors

Average Euclidean distance among the vowels with same base phoneme but different tone	3.5463
Average Euclidean distance among the vowels with different base phoneme but same tone	3.8222
Average distance from the vowels with different base phoneme and tone	4.6514

Table 5 Evaluation metric for the HMM based recognizer

Correctly recognized the tonal vowel	89.23%
Incorrectly recognized as a tonal vowel with same base phoneme but different tone	6.46%
Incorrectly recognized as a tonal vowel with same tone but different base phoneme	2.91%
Incorrectly recognized as a tonal vowel with different tone and different base phoneme	1.40%

instances of each vowel have been used for training and the remaining 40% for testing the system. The performance of the MGD features have been evaluated in terms of recognition accuracy, which is the percentage of times the recognizer has been able to recognize the tonal vowel correctly. The error cases have been further in-depth investigated to get an insight into the confusion created at modeling level. Table 5 presents an analysis of the performance of HMM based tonal vowel recognition.

From the experiments it has been observed that the short-term phase based MGD feature vector is efficient in representing both tone variation as well as base-phoneme variation in case of tonal vowels. Only in the case of 6.46% cases the recognizer has been unable to recognize the tone variation of the same base-phone whereas in 2.91% cases tone takes more dominants over base-phone for tonal vowel recognition. This facts reassures the suitability of MGD feature for tonal vowel recognition in particular and language recognition in general.

5 Conclusion

It this paper we have investigated the performance of MGD features for their tonal vowels discrimination capability. It has been observed that phase-based MGD feature extracted from different tonal vowels is statistically separate from each other in the feature space even when they are different from each other only by tone or base-phone. This fact has been established by statistical measures Euclidean distance and F-ratio test. The performances of the features have been evaluated with a HMM based recognizer in terms of recognition accuracy. In 89.23% cases, the tonal vowels are recognized correctly by the HMM based recognizer trained and tested with MGD features. In the present investigation, it has been observed that MGD features are equally efficient in representing vowels with lexical tone (rising and falling) and vowels without any lexical tone (level tone). This observation appeals more in-depth investigation of the MGD feature for using it as a parameterization technique for language independent ASR system.

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This book discusses important developments emerging around the land questions in India in the context of India's neoliberal economic development and its changing political economy. It covers many issues that have been impinging the political economy in Land and livelihoods in India since the 1990s, examining the land question from diverse methodological standpoints. Most of the chapters rely on evidence generated through primary surveys in different parts of the country. The book, via its diversity of approaches and methodologies, brings out new and hitherto unexplored and/or less researched issues on the emerging land question in India. The range of issues addressed in the volume encompasses the contemporary developments in the political economy of land, land dispossession, SEZs, agrarian changes, urbanisation and the drive for the commodification of land across India. The authors also examine role of the state in promoting the capitalist transformation in India and continuities and changes emerging in the context of land liberalisation and market-friendly economic reforms.

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'land' as a resource and as a commodity, the institutional histories of land management have also created specific challenges for developing an equitable and efficient land policy. Land is also a source of power and wealth in many rural, agrarian contexts. The legacies of unequal access to and control over land are being renewed under the new circumstances, often leading to adverse consequences for traditionally marginalised groups. With the consolidation of neoliberal ideas, the power relations that govern and mediate access to land, mainly through the state institutions, have undergone significant changes. As governments compete with each other to attract domestic and internal capital, the ability to provide land cheaply, with reduced transaction costs, and without much delay has emerged as a critical aspect of being attractive to capital. The challenge of meeting the expectations of capital in an electoral democracy, where those who are involuntarily displaced from their land or livelihoods also have a voice, is formidable. The studies included in this book attempt to explore the unravelling of these questions in India in specific regional contexts.

Most of these studies were initially presented and discussed at a seminar in 2017 at the Indian Institute of Advanced Studies, Shimla. We express our gratitude to the authorities and the staff of the institute for providing us with all the necessary support. The conversations around the theme of land and livelihood continued in the following months, and the chapters have been revised and updated for the volume. We are immensely thankful to the authors who have contributed to the edited volume for their patience and support throughout the process of developing this volume. We are grateful to Prof. Raju Das, York University, Toronto, and the anonymous referees of Palgrave Macmillan whose insightful comments on previous drafts have been helpful to revise the chapters. We appreciate the editorial and academic support of Mr. Krishna Surjya Das, a research scholar at the Centre for the Study of Regional Development, JNU.

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New Delhi, India
Bhubaneswar, Odisha, India

Deepak K. Mishra
Pradeep Nayak

Contents

CHAPTER 15

The Gendered Transformation of Land Rights and Feminisation of Hill Agriculture in Arunachal Pradesh: Insights from Field Survey

Vandana Upadhyay

1 Introduction

The land tenure system in the hill areas of India's north eastern region, inhabited mostly by the tribal population, is significantly different from the system that is prevalent in the plain areas of the region. Like most other parts of India, in the plains of north east region too individual rights over land holdings are transferable and buying and selling of rights is normally not restricted. However, this is not the case in the hill areas where individual rights over land have not taken the form of full property rights in the sense that there are certain restrictions imposed on the transfer of these rights, if not practically possible (Bezbaruah 2007; Mishra 2015b; Mishra and Upadhyay 2017). The non-transferability of holding rights makes the land unsuitable as collateral for the purpose of securing institutional credit to land holders, which in turn acts as a constraint on the

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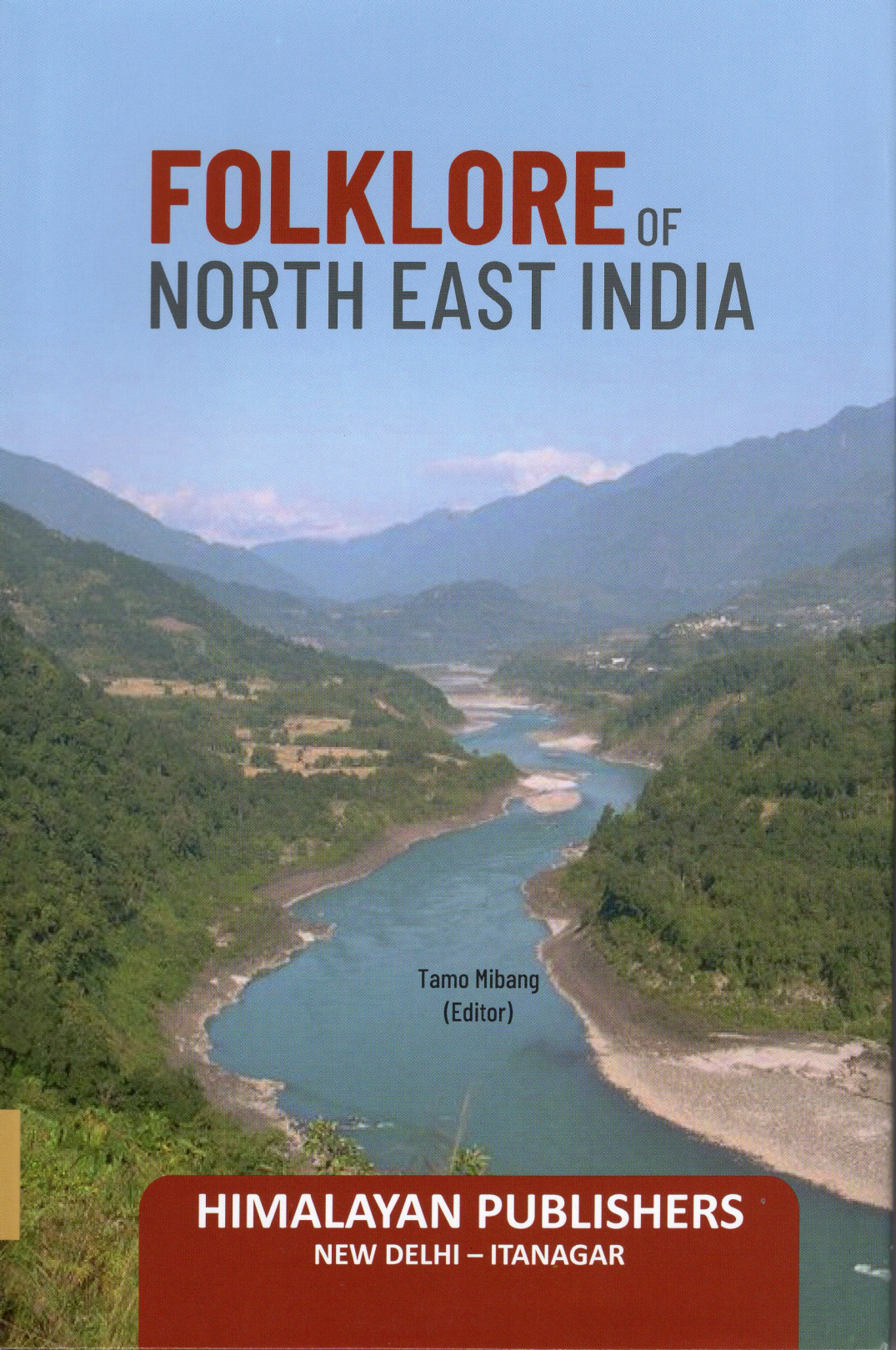

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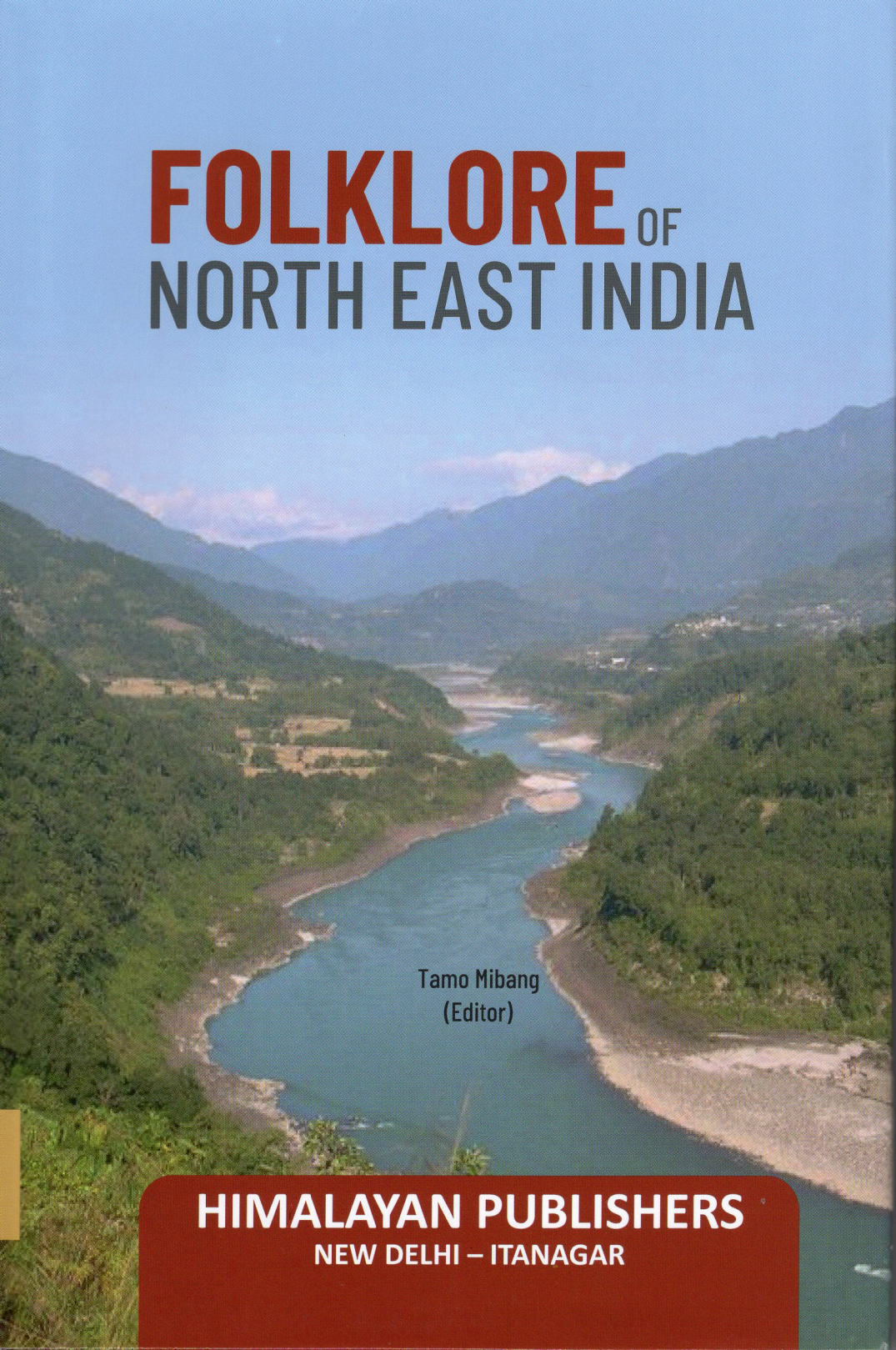

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