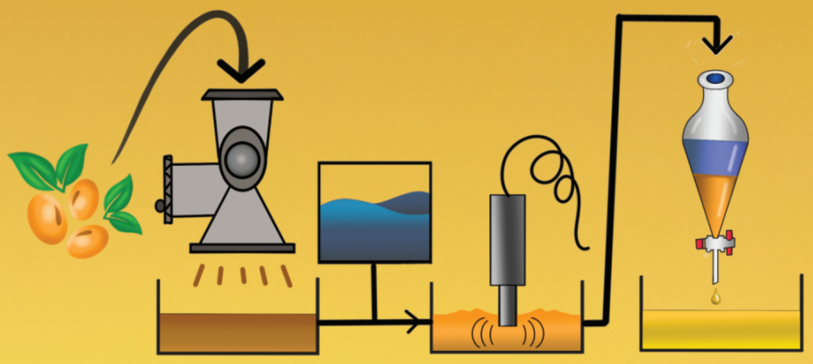
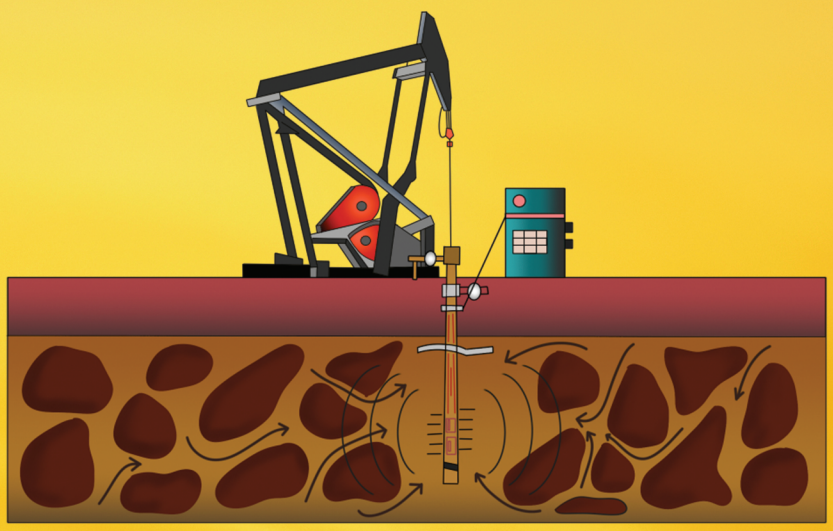
ULTRASOUND TECHNOLOGY FOR FUEL PROCESSING





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Ultrasound Technology for Fuel Processing

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Ultrasound Technology for Fuel Processing

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FOREWORD I

Energy security is a major present-day global issue. As fossil fuel sources are drying up, there is an urgent need to explore alternate sources of energy. Climate change risk due to GHG emissions and global warming is also a global challenge. Green fuels in gaseous and liquid forms offer a simultaneous solution to both problems of energy security and climate change. Alcoholic biofuels such as bioethanol or biobutanol and biodiesel have emerged as potential green liquid transportation fuels. Gaseous biofuels of biogas and biohydrogen can substitute the conventional CNG in vehicles. Blending of petroleum fuels with liquid biofuels is being practised in several developed and developing economies. In addition to achieving a carbon-neutral fuel, this technique can also reduce the economic burden of oil import in developing countries like India. Despite voluminous research and literature in the areas of green fuels, extensive commercial implementation has not been achieved. Major causes leading to these effects are the high cost of substrates, and production techniques that are energy-intensive and lengthy. Intensification of the production processes is a possible solution for these issues. Ultrasound and cavitation have emerged as effective techniques for the intensification of numerous physical, chemical and biological processes. The application of ultrasound and cavitation in fuel processing has also been a research-intensive area. Essentially, ultrasound and cavitation are new techniques for introducing energy into the processing system. These techniques make energies available on extremely small spatial and temporal scales. Marked enhancement in process kinetics, yield, and efficiency has been observed with the application of ultrasound.

Ultrasound Technology for Fuel Processing is an attempt to bring out the state-of-the-art status of ultrasound-assisted and enhanced fuel processes – with special emphasis on green fuels. The authors of this monograph have touched upon almost all aspects – from fundamental to applied – of ultrasound-assisted fuel processing. Starting with the basic principles of ultrasound and cavitation, the authors have included distinct chapters on biohydrogen, biomass pretreatment, solid waste treatment, 2G/3G liquid fuels from biomass, microbes and microalgae. Other topics such as biodesulfurization, biofuel synthesis with hydrodynamic cavitation, enhanced oil recovery and crude oil upgradation have also been explicitly covered through individual chapters.

I am absolutely sure that a comprehensive collection of expertise from diverse facets of fuel processing in this monograph will be a versatile single source of information to the students and researchers of the multidisciplinary fraternity of biorefineries and chemical/petrochemical engineering. In recent years, many books and monographs have been published in the area of ultrasound, cavitation, sonochemistry, and ultrasound-assisted processes. However, this monograph is perhaps the first of its kind that exclusively addresses applications of ultrasound and cavitation for fuel processing. This monograph could also be a good reference book for undergraduate/graduate level courses on process engineering and intensification.

I have known the editor of this monograph, Dr. Sankar Chakma, for many years since he joined the Indian Institute of Technology Guwahati as an M. Tech. student. I heartily commend him on his efforts in collating and compiling expertise on ultrasound-assisted fuel processing and presenting it in a methodical and articulate manner. I feel convinced that this monograph will prove to be a valuable and lasting contribution to the area of fuel processing.

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FOREWORD II

I have known the author Sankar Chakma since his doctoral program and I am well familiar with his interests in the field of ultrasound and cavitationally induced transformations. He developed a keen interest in sonochemistry and cavitation during his early stage of research in the subject and used to frequently interact with me personally and professionally. Sankar has made a significant contribution to the understanding of the mechanism of ultrasound-based advanced oxidation processes (AOPs) and reactions such as transesterification for biofuel synthesis. He has extensively investigated the mechanisms of sono-hybrid processes coupling with the numerical simulation of bubble dynamics. He has made a crucial contribution to the understanding of the basic mechanics of sono-hybrid processes for mineralization of emerging pollutants with the identification of links between chemistry and physics which has resulted in a major process intensification.

I am indeed honoured to write a foreword to this book "Ultrasound Technology for Fuel Processing" edited by Sankar Chakma. I have gone through the contents of the book's chapters and have observed that the chapters are organized in a logical sequence, in terms of topics covered in the book and the methodological approach when ultrasound is used in fuel synthesis and processing. The area of ultrasound and cavitation has been hugely exploited in the field of synthesis of alternative fuels and renewable fuel options such as biofuels (in the form of bioethanol, biohydrogen, biodiesel, *etc.*). The up-gradation of fuels as well as enhanced oil recovery from the non-producing crude oil wells by sending sound waves through the various zones in the natural reservoirs which essentially reduce the effects of boundary layers in oil-water system and also between the oil and solid surface of the pores has been a well-studied area and has shown huge potential. This book will provide all the necessary information from the basic concept of ultrasound and cavitation to its applications in various fields of fuel processing technology. For example, chapters 1 and 2 describe factors that influence sonochemistry and that of hydrogen gas using the sonolysis route, chapters 3 to 6 provide ultrasound-integrated hybrid techniques for the pretreatment of biomasses for enhancing the process yield, chapters 7 and 8 describe the biodiesel production through the transesterification route using cavitation, and chapters 9 to 12 describe the success in enhanced oil recovery and further crude oil processing for upgradation and purification. Thus, the information and knowledge shared in this book will be helpful for the general public, business leaders, regulatory/policy makers and scientists.

My best wishes to the authors and readers of this wonderful book!

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PREFACE

Sonochemistry or the application of ultrasound waves is found to be effective for the intensification of physical, chemical, and biological processes through the cavitation phenomenon which induces chemical (radical generation) and physical (microturbulence, shockwaves, *etc.*) effects in the medium. During the application of ultrasound waves, "hot-spot" is generated leading to extreme conditions in the system such as ~5000 K of temperature and ~1000 atm of pressure within the cavitation bubble. These extreme conditions during the chemical reaction result in the augmentation of the kinetics and overall process yield by several orders of magnitude. Using this technique, the synthesis of biofuels, pretreatment of biomass for biofuel production, and enhanced oil recovery or upgradation of oil are reported to be useful. In this book, the various aspects of ultrasound applications for fuel processing have been described which would be an excellent reference guide for researchers, faculty, and professionals in the field of fuel processing technology including bio-refinery and enhanced oil recovery.

Chapter 1 describes the basic concept and history of ultrasound, the origin of the acoustic wave, and its applications. It also provides information on various process parameters such as ultrasound frequency, intensity, system temperature, and dissolved content in the bubble which influence the cavitation threshold. The modeling and simulation of the radial motion of cavitation bubbles under rectified diffusion have also been covered in this chapter.

Chapter 2 provides information about green production of hydrogen gas through the sonolysis of water. It also describes the influence of various process parameters on hydrogen production with the help of experiments as well as numerical simulation.

Chapter 3 discusses the different pretreatment methods for the production of biofuels such as bioethanol, biogas, and biobutanol. The various pre-treatment methods are explained that are used to break down lignocellulosic biomass, making it more amenable to hydrolysis. In addition to more conventional physical, chemical and biological pretreatment methods, novel 'green' methods reported in the literature are also discussed. Furthermore, the various advantages and disadvantages associated with each method of pre-treatment are discussed, and possible solutions for overcoming negative impacts are suggested.

Chapters 4, 5 and 6 briefly describe the proper utilization of sewage sludge and biomass through the production of alternative and renewable energy. This chapter explains the potential of ultrasound-based techniques for the pretreatment of DSS to enhance biocrude production. It shows how the application of ultrasound can increase the COD solubilization, VS reduction, biogas production during AD, and the process yield of lipid extraction for biodiesel production including the promotion of bioethanol production. The application of ultrasound helps extract lipids from microbial biomass within a short span of processing time. The usage of ultrasonication in the fermentation process can result in enhanced oxygen transfer for aerobic culture, homogenization of biomass for the reduction in clump formation, and faster substrate transfer to biomass.

Chapter 7 summarizes the intensification of biodiesel synthesis and discusses overcoming the heat and mass transfer limitation for the transesterification process. It describes the micro-emulsification and high rate of micro-streaming velocities associated with products from the interaction of ultrasound with the liquid medium, which are highly useful for reducing the mass transfer barrier in heterogeneous phases. The synergy of microwave and ultrasound may help enhance the processing rate on a multi-fold basis compared to the individual effect.

Chapter 8 reviews the basic mechanism of intensified approaches using cavitation, and fundamentals of sonochemical reactors, and finally presents important designs and operational guidelines for maximizing biodiesel yields. In this chapter, various operating parameters of AC and HC have been discussed emphasizing the effect and importance of various parameters in the design of AC and HC reactors.

Chapters 9 and 10 describe the enhanced oil recovery and up-gradation of crude oil with the application of ultrasound and cavitation. The major limitations and techniques for eliminating these barriers by the application of novel techniques of ultrasonic waves have been discussed. The present chapter overviews the ultrasound-assisted cavitation to intensify the cracking of asphaltenes and other heavy hydrocarbon molecules present in the vacuum residual feedstock.

Chapters 11 and 12 briefly describe the different sono-hybrid techniques of ultrasound and cavitation for the removal of sulfur compounds from liquid fuels. These chapters present a critical account of research in different facets of ultrasound-assisted chemical- and bio-desulfurization processes. Concurrent analysis of numerical and experimental results on desulfurization using bio-catalyst and chemical catalysts gives more insight into the actual mechanism of ultrasound on microbial and enzymatic desulfurization processes as well as chemical desulfurization processes.

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ACKNOWLEDGEMENTS

In the past ten years, I have been associated with the field of ultrasound and its applications in various processes for the development and intensification of the field. I have developed a keen interest in sonochemistry and cavitation during my early stages of research. The works done by Prof. K. S. Suslick, Prof. A. B. Pandit, and Prof. V. S. Moholkar in the field of sonochemistry and cavitation have influenced and motivated me significantly to pursue a research career in this particular area. Special gratitude goes to Prof. Moholkar who has encouraged, and supported me in the initial stage and helped me develop a better understanding of the subject area.

I feel obliged to edit this book with the help of my friends and colleagues who have contributed to complete this assignment. The area of ultrasound and cavitation is overwhelming in the area of alternative fuels and renewable energy production such as biofuels (in the form of bioethanol, biohydrogen, biodiesel, *etc.*) and up-gradation of fuels as well as enhanced oil recovery from the well by sending sound waves through the various zones in the natural reservoirs which essentially reduce the effects of boundary layers in the oil-water system; and in between the oil and solid surface of the pores. This book will provide all the necessary information starting from the basic concept of ultrasound and cavitation to its applications in various fields of fuel processing technology. For example, chapters 1 and 2 describe factors that influence sonochemistry and the production of hydrogen gas *via* the sonolysis route, chapters 3 to 6 provide ultrasound-integrated techniques for the pretreatment of biomasses for enhancing the process yield, chapters 7 and 8 describe the biodiesel production through the transesterification process under cavitation, and chapters 9 to 12 describe enhanced oil recovery and further processing of oil for upgradation and purification. Therefore, I do hope that the information and knowledge shared in this book will be helpful to the general public, business leaders, regulatory agencies, and scientists.

Gratitude for the help that I have received from friends, colleagues, and students is acknowledged with deep appreciation. I also acknowledge Vishrant Kumar for helping me to design the cover image of the book. Finally, I express my gratitude to my beloved family members for supporting and encouraging me throughout.

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CHAPTER 1

Basic Concepts of Ultrasound and its Effects on Fuel Processing

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Abstract: Ultrasound-assisted technique is well-known for process intensification *via* chemical and physical changes under the influence of acoustic cavitation. Acoustic cavitation is the phenomenon of nucleation, growth, and collapse of cavitation bubbles into a liquid medium that augments the reaction kinetics and the final process yield. This chapter provides a fundamental and detailed understanding of the acoustic cavitation phenomenon. It includes the history and origin of the acoustic wave and its formation, the concept of cavitation bubbles, bubble nucleation and growth mechanism, cavitation effects, and its types. Numerous process parameters, such as applied frequency, intensity, temperature, dissolved gas content, *etc*., also directly or indirectly influence the cavitation threshold are also highlighted.

Further, the ultrasound's physical and chemical effects involving various chemical and biochemical processes to enhance the process yield are also reviewed. The mode of generation of ultrasound energy and its measurement technique are also briefly discussed. Finally, an overview of modeling and simulation of radial motion of single bubble growth, its oscillation in both ultrasound-assisted and conventional systems, and bubble growth rate under rectified diffusion are also discussed in detail.

Keywords: Acoustic cavitation, Bubble dynamics, Cavitation, Intensity, Oxidation, Ultrasound, Ultrasound power.

INTRODUCTION

Ultrasound refers to sound waves with a frequency higher (> 20 kHz) than the upper audible limit of normal human hearing (20 Hz - 20 kHz). However, the

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upper limit of ultrasound frequency is not clearly defined as it varies with the medium under which it propagates (gases ~5 MHz and liquids ~500 MHz) [1]. Animals use ultrasound technology to communicate through echolocation, *e.g*., dog whistles and bat navigation, by emitting and reflecting the ultrasound wave with a frequency greater than 20 kHz. Rapid technological advancement has further widened its application in detecting and finding underwater objects, such as submarines using the SONAR (sound navigation and ranging) technique. Recently, ultrasound has been widely used in medical imaging as sonography to find the internal body structure, blood vessels, fetal imaging, *etc*., and is also used for non-destructive testing of materials. Richards and Loomis (1927) [2] first used ultrasound in chemical processes to enhance the reaction kinetics. Hereafter, ultrasound has been widely used in other fields of chemistry, material synthesis, process intensification, and improving the reaction kinetics of numerous chemical reactions [3 - 9].

Before the emergence of ultrasound, heat, and pressure were the only potential energy sources for enhancing the chemical reaction kinetics and yield. Acoustic energy produced during ultrasound has been considered as an alternative source to enhance the chemical reactivity, reaction kinetics, and yield of chemical reactions. Longitudinal sound waves travel into the air in the form of compression, and the rarefaction cycle increases its molecular motion by excitation of air molecules. It can be considered a mode of energy generation. The efficient use of energy could be possible if it is generated and used within the system itself instead of an additional system. Two components are essential for generating ultrasound waves; one is the sound source in the form of high-energy vibrations, and the second is the medium in which ultrasound waves can travel. The vibrational energy source relies entirely on transducers that can convert the energy from one form into another, like a loudspeaker which converts the electrical energy into sound energy. Ultrasound transducers are special types that have the ability to convert electrical energy (AC signal) into high-frequency sound waves in the reverse mode. Among various transducers, piezoelectric and capacitive types of transducers are widely used to generate high-frequency ultrasound waves due to their quick response to ultrasound waves [1]. The piezoelectric transducers consist of piezoelectric material of quartz, which is active under the supply of AC signal and vibrates to produce the ultrasound waves.

ULTRASOUND WAVE FORMATION

Any materials such as solids, liquids, and gases possessing elastic properties can transmit the ultrasound wave through the molecules of the medium by communicating with their adjoining molecules and so on. In the case of liquid and

gases, the propagation of the sound waves is in the same direction as of the molecules, hence called longitudinal waves. A spring coiled fixed at one end and given a sharp push at the other end is the best example of a longitudinal wave. However, the waves whose direction is perpendicular to the motion of the particles (in the case of solids) is termed transverse wave (Fig. **1**). The formation of ripples on the water surface is the best example of a transverse wave. Based on the irradiation frequency, ultrasound can be classified into two categories, *i.e.*, low and high-frequency ultrasound waves. Low-frequency ultrasound waves are also called "power ultrasound", and their frequency lies in the range of 20-100 kHz for a power greater than 1.0 W cm^{-2}. The power ultrasound can induce significant changes in material synthesis and chemical processes. Hence, it is commonly used in microbial cell degradation and enzyme deactivation in food processing, surface cleaning, plastic welding, and accelerating the reaction kinetics [5, 10, 11]. On the other hand, high-frequency ultrasound waves (>100 kHz), also called low-power ultrasound, are primarily used in non-destructive analysis; for example, medical imaging, sonography, decontamination of solid substrates in micro-electronic industries, and various other analytical purposes to estimate the velocity and absorption coefficient of the sound wave in the frequency range of 2-10 MHz [1, 12, 13].

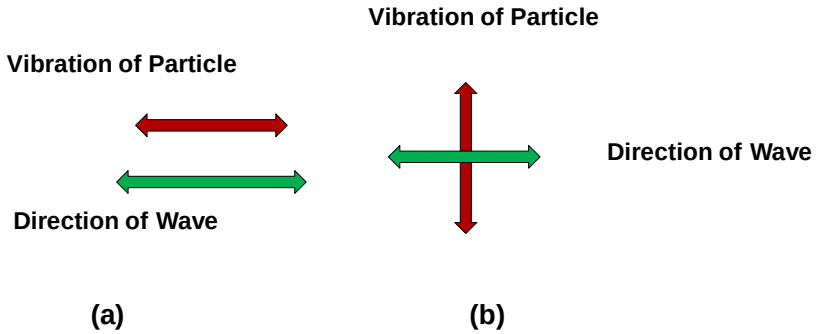

Fig. (1). Movement of wave and particle in (**a**) longitudinal wave and (**b**) transverse wave. (Adapted from Mason and Lorimer, 2002) [1].

ULTRASOUND WAVE PROPAGATION

Before proceeding to the discussion on the acoustic phenomenon that occurs in the liquid medium, herein, we first focus on the propagation of sound waves into the air medium. It can provide better information for understanding the ultrasound wave phenomenon and its propagation in the liquid medium. When sound waves propagate through the air medium, the air molecules get displaced under the influence of sound energy, and at any time (t), the displacement (y) of air molecules from their mean rest position can be given according to the following equation:

CHAPTER 2

Sonochemical Production of Hydrogen: A Green and Sustainable Approach

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Abstract: In the last two decades, the subject of hydrogen production by sonolysis (sono-hydrogen) has been widely investigated experimentally and theoretically. This chapter highlights the recent experimental and theoretical progress in the field of sonochemical production of hydrogen. The chapter will be divided into two parts: (i) literature review of the available experimental data (experimental conditions, production yields, influencing factors) and (ii) a numerical analysis of the treated subject, with emphasis on the impact of different energetic terms of the bubble energy balance on the sonochemical yields of hydrogen, all with relation to operational parameters (frequency, intensity of ultrasound, size of bubble population). The chapter will be closed with some perspectives on innovation and sustainability of the process.

Keywords: Acoustic bubble, Power ultrasound, Sono-hydrogen, Water sonolysis.

INTRODUCTION

Cavitation sonochemistry is considered as one of the important events (such as sonoluminescence, shock wave *etc.*) taking place upon the interaction of ultrasonic irradiation with tiny bubbles [1]. Several radicals (*e.g.* •OH and HO_2•) and active species (*e.g.* H_2O_2) are generated at the end of bubble collapse due to the extreme conditions of temperature and pressure (around 5000K and 1000atm) [2]. Recently, the sonochemical production of hydrogen has attracted the attention of many researchers as a clean, non-toxic and low cost method [3 - 12]. As one of the promising future's energy carriers, hydrogen has paramount advantages [*e.g.* HHV (higher heating value) and LHV (lower heating value) are 141.9 KJ g^{-1} and 119.9 KJ g^{-1} [13], respectively, different forms of storage (*e.g.* liquid, gaseous or

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in together with metal hybrid), abundance, a clean fuel with no CO_2 emissions and can be used in fuel cells for generation of electricity [14 - 16] compared to the other traditional sources of energy (methane, gasoline, diesel, ethanol and methanol).

The sonolytic generation of hydrogen can be intensified using many additives either in the gas matrix or in the sonicated water. For instance, the addition of hydrocarbons such as methane and ethane provokes a drastic enhancement in hydrogen generation [17]. Methane and ethane can penetrate into the hot gas phase of the bubble and their pyrolysis yielded excessive amounts of hydrogen [17]. Correspondingly, alcohols such as methanol play the same role as CH_4 following the same pyrolytic reaction mechanism inside the bubble [18, 19]. However, the concentration of these additives should be controlled as too high a concentration could decrease the yield of hydrogen production. On the other hand, hybrid techniques (sonocatalysis, photosonolysis and sonophotocatalysis) are emerging for the enhancement of sono-generation of hydrogen. Therefore, serious works should be conducted in order to improve our understanding and effectiveness of the different sonochemical methods [20, 21].

The present chapter exhibits the recent experimental advancements in the sonolytic production of hydrogen as well as the different parameters affecting this process. In addition, the available works focusing on sonocatlysis, photosonolysis and sonophotocatalysis production of H_2 are discussed in comparison with the sonolysis. In the second part of this chapter, the effects of the different transfer phenomena (mass transport, heat exchange and reactions heat) on sono-formation of hydrogen are discussed. These impacts are treated according to the size distribution of active bubbles, variation of ultrasound frequency and acoustic intensity.

THE PRINCIPAL OF SONOCHEMISTRY

Acoustic cavitation is the central event of ultrasound (20-1000 kHz) propagation in liquids. Practically, this event is responsible for all physical, chemical and biological effects of sonication [22 - 27]. Fig. (**1**) depicts the basic processes of sonication and sonochemistry. The principal steps are:

A. When the ultrasound waves with high frequency pass through liquid water, it will lead to severe vibrations of water that result in generating acoustic cavitation bubbles. Intense ultrasonic waves within the frequency range from 20 to 1100 kHz traveling through liquids trigger small acoustic cavities that grow, oscillate, growth, and implode in a sequence, creating a tremendous amount of heat within the bubble.

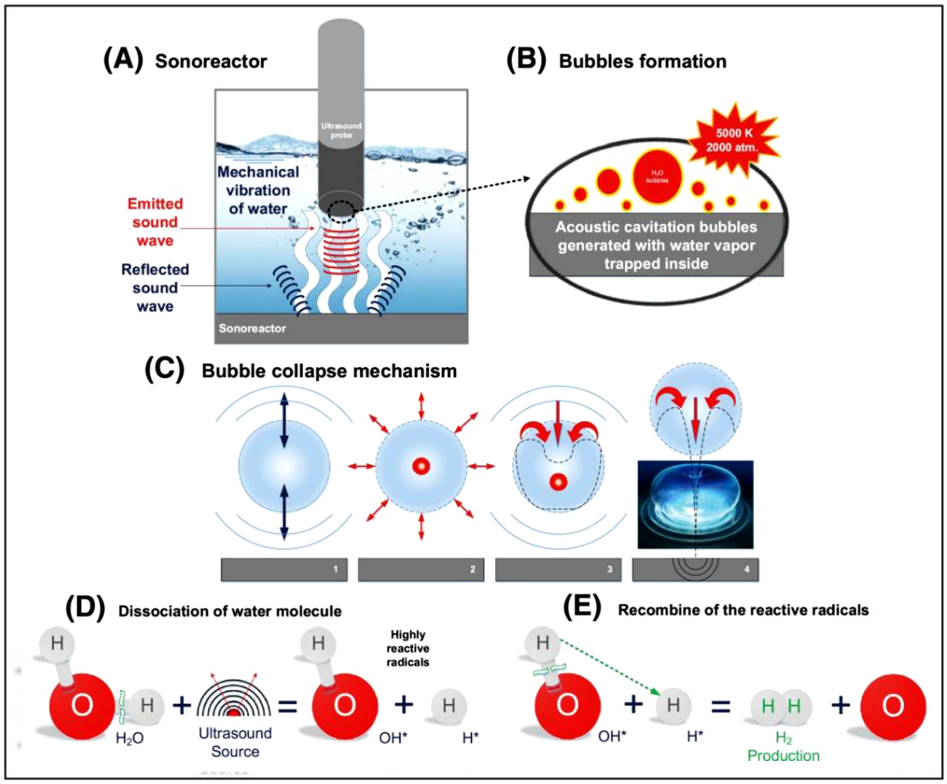

Fig. (1). Schematic representation of water sonication, bubble collapse and bubble sonochemistry [3, 111].

B. In homogenous reaction systems, the growth of bubbles in an appropriate size range (initial cavitation bubbles) occurs by a process known as rectified diffusion. This happens when the acoustic pressure is above a certain threshold. The growth of a bubble by rectified diffusion results from the uneven mass transfer rate across the air-liquid interface. The cavitation bubble repeats expansion and contraction according to the acoustic cycle. If the pressure amplitude is above the cavitation threshold, the bubble collapses rapidly and provides extreme conditions of several thousands of Kelvins, several hundred atmospheric pressure and heating and cooling rates greater than 10^9 K s^{-1}.

C. Near solid surfaces, the cavitation bubble collapses in an asymmetric manner. The two important mechanisms responsible for the effects of cavitation in solid-liquid mixtures are shock wave damage and microjet impact [22]. These phenomena can arise when a cavitation bubble implodes near a solid surface, asymmetric cavity collapse. During a collapse, a cavity deformation is self-reinforcing and simultaneously a stream of fast-moving liquid directed to the solid surface is produced, which is named microjet [28]. The microjet's speed is

CHAPTER 3

Physical, Chemical and Biological Pre-treatment of Lignocellulosic Biomass for Biorefinery Applications

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Abstract: The generation of energy from fossil fuels contributes significantly to global warming. This may be mitigated by the use of renewable (bio-based) feedstocks. Second generation biofuels made in biorefineries that utilize agricultural residues and other lignocellulosic wastes as feedstocks reduce the dependency on food crops such as sugar cane (for bioethanol) and oil seeds (for biodiesel). Pre-treatment of lignocellulosic feedstocks is key for ensuring process efficiency from the substrate to the product. There are many pre-treatment methods, and method selection is incumbent on the type of feedstock and the downstream processes required to generate the final product(s). Product yields can be increased by integrating two or three pre-treatment methods. For example, by combining physical and/or chemical pre-treatment with ultrasonication. The content of this chapter is focused on describing various pre-treatment methods that are used to break down and/or hydrolyse lignocellulosic biomass. The discussion extends to both conventional and novel 'green' methods and includes the advantages and disadvantages of each method type. Possible solutions for overcoming some of these disadvantages are included.

Keywords: Biorefinery, Feedstock, Lignocellulose, Pre-treatment.

BACKGROUND

Lignocellulosic biomass is readily available, inexpensive and renewable, making it one of the most promising feedstocks for biorefineries. In the context of a circular economy, agricultural wastes and residues are abundant sources of lignocellulose. Lignocellulose itself contains a number of valuable substrates, including sugars and proteins that can be transformed into value-added products by microbial species. To facilitate downstream processing, the lignocellulose first

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needs to be fractionated so that microbial enzymes can access the substrates. This is achieved by physical (mechanical, thermal, ultrasonic), chemical, or biological pre-treatment processes. To maximize substrate availability in the most efficient manner, different treatment methods are often used in conjunction with one another. In order to select the best form/s of pre-treatment for each particular feedstock, it is imperative that the lignocellulosic degradation mechanism/s are well elucidated.

Lignocellulosic biomass is typically composed of three main components *viz*, cellulose, hemicellulose, and lignin. Cellulose and hemicellulose are carbohydrate polymers, while lignin is a non-carbohydrate phenolic polymer and is more recalcitrant to biodegradation. Lignin is not readily utilized as a microbial substrate and needs to be removed *via* pre-treatment to release the hemicellulose and cellulosic moieties. Celluloses are strong crystalline polymers that account for 30-50% of plant dry matter. They consist of linear chains of β (1→4) linked D-glucose units which are resistant to hydrolysis. Hemicelluloses are amorphous heteropolymers (arabinoxylan, glucuronoxylan, xyloglucan, glucomannan) with lesserstrength and account for 15-30% of the cell walls of plants. They may originate from pentose sugar (xylose and arabinose) or hexosesugars (galactose, rhamnose and mannose). Hemicelluloses that are primarily comprised of D-xylose dominate in agricultural wastes and residues [1]. However, cellulose is targeted for many fermentative processes because glucose is such a versatile microbial substrate.

Lignin is considered to be the 'cement' in plant cell walls as it fills the spaces between cellulose, hemicellulose and pectin. Cellulose and hemicellulose are strongly bonded to lignin through covalent and hydrogen linkages. The crosslinked nature of these bonds provides mechanical strength and hardness to the cell walls of plants but may render the biomass resilient to pre-treatment [2]. One of the biggest challenges for commercial lignocellulosic biorefineries is to find cost-effective and efficient pre-treatment technologies that deconstruct the biomass with negligible sugar loss and generation of inhibitors [3]. This chapter provides a global overview of the pre-treatment techniques currently in use, and those that show promise for future implementation.

PHYSICAL PRE-TREATMENT

The application of intricate raw lignocellulosic feedstocks in biorefinery systems requires an initial essential step of physical pre-treatment to reduce the size of the biomass and increase the effective surface area. It can also reduce the crystallinity of complex sugars, thereby assisting with digestion. However, physical pre-treatment does not significantly alter the chemical structure of the cell walls.

Lignin remains intact after physical pre-treatment, so it cannot be used as a stand-alone method [4]. Dissolution of lignin can be successfully achieved by subsequent chemical and/or enzymatic hydrolysis of biomass. Widely used physical pre-treatment methods include mechanical comminution, physico-thermal treatment, electrochemical treatment, and ultrasonication. Physical and mechanical pre-treatment methods are the most environmentally friendly from a waste generation perspective, as they neither utilize harmful chemicals nor result in the production of byproducts. However, to achieve complete degradation of lignocellulosic biomass, physical methods need to be coupled with chemical or biological hydrolysis to maximize sugar release. Table **1** displays the cumulative effects of some physical, chemical and enzymatic hydrolysis methods on the conversion of a range of relevant feedstocks into value-added products. In below subsections, upstream and downstream physical pre-treatment methods are described. Many of these can be complemented by ultrasonication, which is also a physical method, to enhance the overall effectiveness of pre-treatment.

Table 1. Cumulative effect of various physical pre-treatment methods assisted with chemical and enzyme hydrolysis for bioconversion of biomass into bioproducts.

Substrate	Physical pre-treatment	Chemical and/or Enzyme Pre-treatment	Key Outputs	Refs.
Wheat straw	Ball milling	*Chemical:* Mild alkali (Aq. NaOH) *Enzyme:*Cellulase (Cellic CTec2™)	*Sugars:* 93.8% hemicellulose and 86.1% lignin removal. 98.5% glucose yield.	[23]
Barley straw	Manual cutting, Szego Mill™ (dry milling, wet milling &N_2-assisted wet milling)	*Enzyme:* β-glucosidase (Accellerase™)	*Ethanol:* 3.4 to 6.7gL^{-1} from 1.7 gL^{-1} glucose. *Biogas:* 6–11% increase in CH_4 generation rate.	[12]
Rice straw (RS)	Planetary milling, attrition milling, autoclaving (15 psi, 15 min, 121°C)	*Chemical:* Aq.NH_3 *Enzyme:* Cellulase cocktail (Worthington Biochemical Co., USA)	*Sugars:* Enhanced sugar yield by reducing RS crystallinity from 0.48 to 0.11 and lowering soluble phenolics.	[24]
Palm oil biomass	Compressed hot water (150–190°C, 10–240 min) with wet disk milling	*Enzyme: Acremonium* cellulase (Meiji Seika Co,Japan), and Optimash BG®	*Sugars:* 88-100% sugar yield.	[18]
Corn cobs	Grinder & ball mill	-	*Substrate for biohydrogen generation:* Increased cellulose and hemicellulose release. Reduced activation energy.	[25]

CHAPTER 4

Ultrasound Based Integrated Technique for Production of Sustainable Bio-crude from Domestic Sewage Sludge for Biorefinery

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Abstract: Generation of a tremendous amount of domestic sewage sludge pushes society to look for an alternate and viable option rather than its direct disposal. The organic-rich constituents of sludge make it an asset rather than waste. Sludge to energy conversion is a feasible option to combat the demand for renewable energy. Resource recovery from waste leads to socio-economic development by reducing fossil dependency with clean and green energy. This chapter mainly focuses on the potential of ultrasound-based techniques for the pretreatment of DSS to enhance bio-crude production. Thermochemical and biochemical treatment are two routes of sludge valorization with their advantages and limitations. Pyrolysis, gasification, combustion, and hydrothermal processing come under thermochemical treatment whereas, anaerobic digestion, aerobic digestion, and fermentation form the basis of biochemical treatment. Thermochemical routes demand energy, whereas biochemical routes are a time-consuming process. Pretreatment of sludge is a viable option to overcome these limitations. Ultrasound pretreatment increases COD solubilization, volatile suspended solids reduction, biogas production during AD, increases the yield and HHV of bio-crude during thermochemical treatment, and favors lipid extraction for biodiesel production, and also promotes bioethanol production. Moreover, integrated ultrasound pretreatment positively affects the overall process by reducing the overall cost and increasing bio-crude production.

Keywords: Biochemical conversion, Bio-crude, Biorefinery, Cavitation, Domestic sewage sludge, Thermochemical conversion, Ultrasound pretreatment.

INTRODUCTION

Rapid urbanization and population explosion lead to a considerable amount of sewage that creates undesirable challenges related to waste management. Sewage

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contains above 99% of water where solid waste, oils, and grease are in suspension. Wastewater treatment plant treats this sewage to remove the contaminants as sludge for safe disposal of the treated water. Hence, sewage sludge (SS) is a solid, semi-solid or liquid by-product obtained from a sewage treatment plant. Domestic sewage is collected from households, institutional and commercial establishments, and includes proteins, sugars, detergents, pesticides, coloring solvents, phenols, lipids, some toxic and hazardous organic and inorganic pollutants [1, 2]. The presence of heavy metals, harmful viruses, and bacteria make the direct disposal of sludge not feasible as it causes health hazards, economic constraints, and secondary pollution [3, 4].

In a wastewater treatment plant, the sewage is treated in several subsequent stages. In the preliminary stage, heavy and coarse materials (diameter of more than 2 cm) are removed by screening. Water from the preliminary treatment stage enters the primary treatment, where fine and hard solids are removed. Suspended solids, oil and grease (scum), and settleable solids are recovered from the primary treatment stage. The primary sedimentation tank or clarifier is used to sediment girt particles (fine and hard solids). In the secondary treatment process, water from the primary treatment is treated to remove the biodegradable materials. The dissolved and suspended organics are consumed by microorganisms. The aerobic and anaerobic fermentation process produces valuable fuels like CO_2 and biogas, along with volume reduction. A tertiary plant treated the water from the secondary plant for improving the quality of discharge water into the environment. Sludge can be classified as primary, secondary, and mixed sludge depending upon the source from where the sludge has been collected [1].

Primary Sludge: Precipitated solid and floated oil, grease, and lighter solids removed from primary clarifier/sedimentation basins during primary sewage treatment is the primary sludge [1, 5].

Secondary Sludge: Secondary treatment introduces microorganism that removes biodegradable material present in primary sludge such as food waste, human waste, soap, detergents, *etc.* The sludge obtained from secondary treatment is known as biological sludge, secondary sludge, and waste activated sludge (WAS) [1, 5].

Mixed Sludge: It is a mixture of primary and secondary sludge in the desired proportion [1, 5].

The conventional method of SS disposal includes direct incineration, landfilling, agricultural application, and composting. The sludge is composed of organic and inorganic fractions. A significant portion of organic fractions includes extracellular polymer substrates (EPS), and it counts the proteins, lipids, nucleic

acid, humic substances, and polysaccharides. Heavy metals, pathogens, and nitrogen from human diets find their way into domestic sludge are the inorganic portion of SS [6]. The primary objective of sludge is to reduce the sludge volume by adopting some environmentally friendly processes. With the growing demand for energy generation from renewable sources, the organic-rich sludge cannot be considered a waste. Instead, the valorization of sludge into bio-crude solves the problem of sludge disposal. It leads to socio-economic development by reducing fossil dependency with clean and green energy. Thermochemical and biochemical are two techniques for sludge valorization, both having their advantages and limitations. Bio-crude from the thermochemical process is not suitable to use as transportation fuel owing to high oxygen and water content, high viscosity, *etc.* For biochemical processes, higher retention time, low degradation efficiency, and a narrow range of products are some limitations. Pretreatment of SS prior to conversion may bridge the gap of bio-crude upgradation for a sustainable biorefinery [6]. Pretreatment methods of SS include physical/mechanical, chemical, thermal, and biological pretreatment. US pretreatment, which falls under mechanical pretreatment, is a green and clean approach for intensifying biofuel production from SS. Enhancement in sludge solubilization and biodegradability during US pretreatment, triggers the bio-crude production from sludge through different valorization methods [4, 7].

This chapter mainly focuses on US pretreatment of SS for quantification and quality upgradation of bio-crude from thermochemical and biochemical conversion for a sustainable biorefinery. Starting from the different valorization routes of sludge and different pretreatment methods available, this chapter explains the US mechanism and the influence of operating parameters on the sludge properties. It also emphasizes the integrated pretreatment methods for enhancing bio-crude production. A comparison is shown in tabular form to highlight the advantages of the US and integrated US-based approach over non-treated sludge.

VALORIZATION ROUTE FOR SUSTAINABLE BIO-CRUDE PRODUCTION FROM SEWAGE SLUDGE

Thermochemical Routes

Thermochemical treatment of domestic sewage sludge (DSS) is an emerging technology with great potential for recovery of energy. Production of fuels/chemicals from SS reduced sludge volume, and destruction of harmful pathogens. It includes combustion, pyrolysis, gasification, and hydrothermal processing. Thermochemical treatment shown in Fig. (**1**) is an energy-intensive process that demands high capital and running costs [6, 8].

CHAPTER 5

Application of Sonication in Lipid Extraction from Microbial Biomass for Third Generation of Biodiesel

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Abstract: Increasing demand in terms of fuel and energy with limited fossil fuels forces researchers to develop renewable fuels in sustainable ways. Biodiesel, as an alternative to mineral diesel, has emerged as one of the potential renewable fuels. With an increasing demand for biodiesel, conventional and non-conventional sources of triglycerides were investigated. In terms of future demand, edible and non-edible sources are insufficient to fulfill the requirement and thus microbial oil will be one of the crucial feedstock for biodiesel production. The extraction of lipids from various biomass is one of the crucial steps in the synthesis of biodiesel, which controls the overall production cost. Over the last few years, conventional lipid extraction techniques such as solvent extraction, mechanical processes, and chemical treatments have been explored, however, all these have their own limitations. Moreover, in order to obtain high purity lipids in an economical way, the use of sonication has garnered much attention in extracting the lipids from the microbial biomass because of the shorter process time, the straightforwardness of the process, and the superior quality of products. It may also lead to reducing the use of solvents in the extraction process. The book chapter deals with the limitations of conventional extraction processes of lipids from microbial biomass and the role of ultrasound in efficient and economic operations. Moreover, to lower the production cost, the application of ultrasound in simultaneous extraction and transesterification has been explored.

Keywords: Biodiesel, Extraction, Lipids, Microbial biomass, Transesterification, Ultrasound.

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INTRODUCTION

The limited amount of fossil fuels and unceasing increase in demand for fuel and electricity, along with environmental legislation, force the researchers to search for alternate routes of producing fuel and electricity in an environmentally friendly manner [1]. In the search for an alternate liquid transportation fuel, ethanol, butanol and biodiesel have gained the attention of researchers globally. Among these liquid biofuels, biodiesel has come up as a prominent alternative to mineral diesel due to its ease of handling and lesser production cost, as compared to bioethanol and biobutanol [2 - 4]. Biodiesel has numerous advantages over mineral diesel, *viz.* higher flash point, superior viscosity, sulphur-free fuel and many more, which explains its selection as an alternative to mineral diesel in a compression ignition engine over the other two biofuels [5 - 8]. Biodiesel can be used in pure form or blends with the mineral diesel [7]. Chemically, biodiesel is a mixture of fatty acids methyl esters, which can be obtained through vegetable oils (edible and non-edible), waste cooking oils, animal fats, and microbial lipids [9 - 11]. Most of the commercial biodiesel producing units throughout the world utilize edible oil as a starting raw material. The selection of edible oils for the production of biodiesel is advantageous in terms of higher biodiesel yield with shorter reaction time. On the other hand, the diversion of edible oils for biofuel production leads to the "food *vs.* fuel" debate and also increases the overall production cost of biodiesel [2, 3, 6]. On the whole, the feedstock used for biodiesel production contributes to around 60-90% of the overall production cost [12]. In view of the increasing biodiesel demand with limited arable land, the non-edible oil resources and microbial lipids will be the starting material for biodiesel in upcoming years [6, 7, 13 - 16]. The increasing population and its corresponding demand for food and shelter will not allow for the diversion of arable land or deforestation for the growth of non-edible oil crops [16, 17]. In order to fulfill the future demand for energy without deforesting the land, lipid-rich organic resources have been explored by researchers for the production of biodiesel. The microbial biomass can be grown on ponds (stagnant water sources) or non-fertile lands. In contrast to this, the lipid content of microbial biomass is very limited and the associated excess water makes it a difficult and expensive process for direct use in biodiesel production [16, 18]. Recently, many researchers have attempted to convert the microbial lipid into biodiesel using the co-solvent method, the supercritical solvent method as well as the application of biocatalysts to improve the conversion of fatty acids into esters [19 - 25]. The key or primary limitation in the microbial lipid to biodiesel conversion is the extraction of lipids from the microbial biomass. The water present in the biomass limits the extraction of lipids; and hence, more research is required in cost efficient extraction processes. Researchers have explored various methods such as mechanical, chemical, solvent extraction, *etc.* [6, 16, 22]. In the subsequent sections, different

types of microbial biomass and their lipid content are discussed. This chapter mainly focused its discussion on the effect of sonication on the improvement of lipid recovery and improvement in the biodiesel yield thereof.

MICROBIAL BIOMASS – A POTENTIAL RESOURCE FOR BIODIESEL

Basically, biodiesels are the fatty acids methyl esters. As stated in the introduction, they can be synthesised from vegetable oils, animal fats, and microbial lipids, by reacting them with short-chain alcohols [2, 6, 7, 9, 15, 22, 26]. Based on the feedstock selected for biodiesel production, biodiesel is roughly categorized into different generations. The biodiesel produced using edible vegetable oils (typically, negligible free fatty acids and no water content) are categorized as 1st generation biodiesel. Similarly, the biodiesel synthesized using non-edible vegetable oil, waste cooking oil and animal fats such as waste tallow, lard, fat, *etc.* (nominal free fatty acids without water content) falls under 2nd generation biodiesel and the biodiesel produced using oleaginous organic biomass-derived lipids such as macro and micro algal, yeast, and fungi are termed as 3rd generation biodiesel [3, 6, 7, 16, 27, 28]. The 3rd generation biodiesel is still under research as the total contribution of 3rd generation biodiesel is less than 1% as compared to 98% for the first generation and ~ 1.5% for second generation biodiesel. In upcoming years, however, it will be an important contributor to meeting the future demand. Oleaginous biomass can be grown on ponds, waste water treatment units, and saline water, and thus, has a unique advantage over the first and second generation biodiesel feedstock [16, 17, 22]. Oleaginous biomass such as algae, yeast and fungi is the important oil producer of the future.

Algae for Biodiesel Production

Algae are photosynthetic microorganisms with diverse groups of various strains. Algae (more specifically microalgae) utilize solar energy and carbon dioxide (CO_2) and convert them into lipids, proteins, carbohydrates and traces of pigments [29, 30]. The growth cycle of algae is short and rapid, but most of the strains that grows in the open atmosphere have very low accumulations of lipids, proteins and carbohydrates [31, 32]. To improve the lipid, protein, and carbohydrate contents, the stains of the microalgae are mutated, and parameters that have a direct effect on the rate of photosynthesis such as temperature, and sunlight intensity, are optimized and controlled in specially dedicated bioreactors [30, 32]. Therefore, large-scale microalgae cultivation can be done in a controlled environment either through open ponds or through closed bioreactors [32]. Many researchers have identified different strains of microalgae and optimized the parameters to improve the cell biomass density, as well as specific growth rate, using earmarked

CHAPTER 6

Application of Ultrasound in Microbial and Algal Biofuel Production

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Abstract: The application of ultrasound has received immense research attentions in the past few years due to its application in various sectors including dye degradation, pretreatment process, fuel production, bioprocessing, *etc.* Recently, ultrasonication has been used as a novel bioprocessing tool for enhancing biofuel production from microbial and algal biomass during the fermentation process. Additionally, this technique is also used in many areas of downstream processing such as extraction of lipids from biomass, filtration, and crystallization. The usage of ultrasonication during the fermentation process can result in the enhancement of the transfer of oxygen for aerobic culture, homogenization of biomass for the reduction in clump formation, and faster substrate transfer to biomass which further results in enhanced microbial growth. In view of this, the present chapter mainly focuses on the role of ultrasonication in microbial and algal lipid production and its extraction process with an aim for liquid biofuel production. Additionally, the influence of various operating parameters (power intensity, frequency, duration, reactor design, and kinetics) over the growth, lipid production, and extraction process are also described in detail.

Keywords: Algae, Extraction method, Low–cost substrates, Oleaginous microorganism, Single cell oils (SCOs), Ultrasonication.

INTRODUCTION

With increasing demand for energy due to higher population growth rate, and constant depletion of fossil fuel reserves, the necessity for bioenergy has been constantly increasing over the years. Additionally, the increase in fossil fuel cons-

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umption has led to numerous environmental implications, including greenhouse gas (GHGs) emissions, climate change, energy security, *etc.* Hence, the primary research and developments are focused on the production and application of bioenergy which can mitigate the issues related to fossil-derived fuels. As per the recent report, the share of renewables in global electricity generation reached approximately 27% in 2019 [1]. Bioenergy from renewable sources such as solar, wind, and biomass have been given new hope for sustainable future applications. One of the bioenergy components also includes biofuel which has attained greater attention due to its sustainability and environment-friendly nature. The biofuels are primarily classified into solid, liquid and gas which are produced by biological or thermochemical conversion of renewable substrates such as lignocellulose waste, food waste, wastewater, *etc.* [2]. Further, these biofuels are categorized into different types such as first-generation, second-generation, third-generation, and fourth-generation based on the origin of raw materials used in the production process [3]. More details about its source with examples are given in Fig. (**1**).

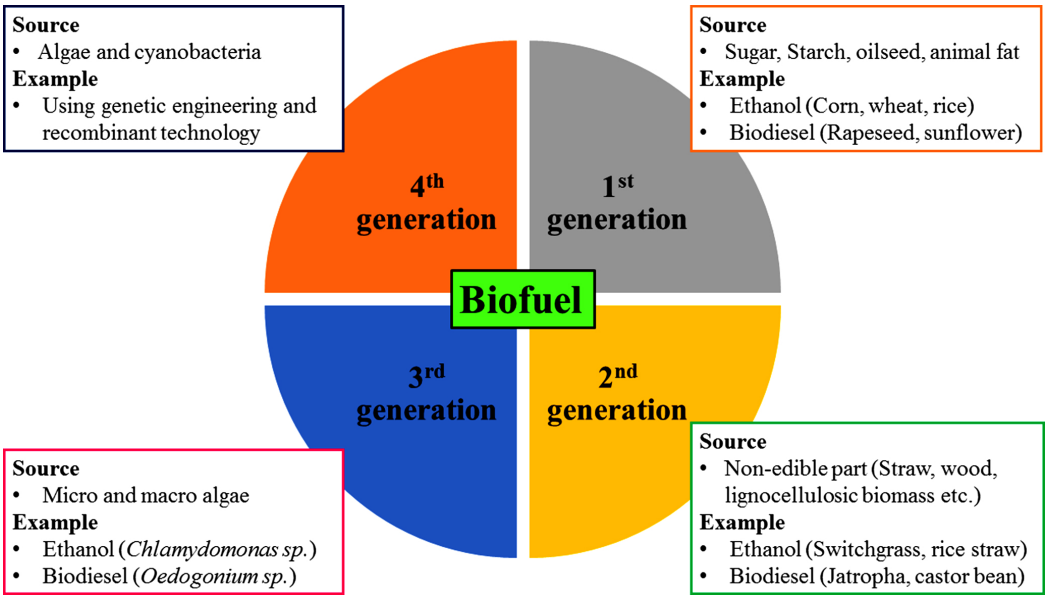

Fig. (1). Classification of biofuel with example.

The use of non-edible feedstock such as lignocellulosic biomass (wheat straw, rice straw, sugarcane bagasse, *etc.*) and industrial organic waste for biofuel production provides a promising opportunity by reducing the environmental hazards associated with these wastes and to overcome the limitations associated with the direct use of edible parts for this process. The biological conversion

process holds several advantages over other approaches in terms of environmentally friendly, less energy-intensive, devoid of expensive catalysts, *etc*. Therefore, the current chapter focuses on the conversion of renewable substrates for the production of biofuel by using biological methods. Among several biofuels such as ethanol, butanol, biohydrogen, and biodiesel, the current chapter covers the influence of ultrasound in biodiesel production specifically on microbial or algal lipid production.

Among several alternative sources for biofuel production, biodiesel production using microbial lipid is a promising technology due to its sulfur-free, biodegradable and non-toxic nature [4]. Additionally, biodiesel emits 67% less hydrocarbon, 48% less carbon dioxide, and 47% less particulate matter on combustion than petroleum diesel [5]. Single cell oils (SCOs) or microbial lipids are intracellular storage lipids produced by several oleaginous microorganisms like bacteria, fungi, yeast, and microalgae while utilizing various carbohydrates, crude oils, and hydrocarbons as substrates [6]. These microorganisms accumulate 20 to 80% of lipid per dry biomass under nitrogen and phosphorous limitations while the presence of an excess amount of carbon in the nutrient media. The SCOs are mainly comprised of triacylglycerols (TAGs) and the fatty acids profile of SCOs dependent upon the type of oleaginous microorganism used in the production process. The accumulated microbial lipid or SCOs can be further used for the production of biodiesel *via* direct or indirect transesterification reaction [7 - 9]. Though several studies reported biodiesel production using transesterification, the use of microbial or algal lipid for this process is a relatively new technique developed in the last decade. The increasing demand for biofuel has intended to boost its productivity by adopting several strategies such as optimization of fermentation medium components and process conditions, strain development, isolation of novel strain, *etc*. Nevertheless, the scale-up of production posed several difficulties in terms of control, mixing, and mass transfer, which further decreases the concentration of final product and experiences higher downstream processing costs during product purification [10]. To overcome these issues, ultrasonication has been applied recently as an alternative technique or in combination with other conventional methods for process intensification in several biological processes. Several previous studies [11 - 15] reported the use of sonication in various chemical and biological intensification processes. In addition to the fermentation process, sonication/ultrasound is also applied in several other biological processes such as disinfection, microbial cell disruption, improvement of biological wastewater treatment, crystallization, emulsification, *etc*. [16]. Considering this importance, sonication has been applied in several sectors including the food, pharmaceutical, and biotechnology industry [17, 18].

CHAPTER 7

Synergy of Microwave and Ultrasound for Intensification of Biodiesel Synthesis

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Abstract: Biodiesel synthesis from sustainable feedstock is gaining importance in depleting crude oil feedstock and addressing greenhouse emission challenges. A developing country like India has planned to reduce its 10% dependency on crude oil by 2022. Synthesis of biodiesel from sustainable edible feedstock has been a concern for energy *vs*. food issues. Non-edible feedstock such as *Calophyllum innophyllum Linn*, Karanja, Jatropha, Waste Cooking oil, waste engine oil, *etc*., is gaining importance. However, biodiesel synthesis from these feedstocks requires higher processing due to higher initial free fatty content. Intensified techniques can overcome the shortcoming of higher processing requirements. Spectacular effects associated with ultrasound and microwave are beneficial for enhancing the rate of processing. Individual results of microwave and ultrasound have certain limitations. The intensification of biodiesel synthesis is dependent on the removal of heat/mass barriers in the transesterification process. Microwave interaction with polar molecules present in the system enhances the temperature of the reaction at a very intense rate. Micro-emulsification and the high speed of micro-streaming velocities produced from the ultrasound during interaction with the aqueous phase are incredibly useful for reducing the mass transfer barrier in heterogeneous phases. The synergy of microwave and ultrasound may help enhance the processing rate on a multi-fold basis. The present chapter has presented an overview of microwave and ultrasound energy effects for biodiesel synthesis. Process economics has been discussed for future development in biodiesel synthesis.

Keywords: Biodiesel synthesis, Microwave, Non-edible feedstock, Synergetic effect, Ultrasound.

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INTRODUCTION

In the last few decades, there has been widespread concern about environmental problems due to greenhouse gas emissions from automotive vehicles. There is a need to replace fossil fuels with cleaner renewable energy and develop alternative intensified technologies for biodiesel production [1, 2]. Automobiles consumed more than 30% of petrol-fuels. It contributes maximum component of micro particulate pollutants in environment [3 - 5]. The world-side crude oil status is shown in Fig. (**1**) [5 - 9]. Research on the substitute of clean alternative energy for existing automotive applications is gaining keen interest among the scientific community. Fuel derived from renewable/sustainable feedstock is a promising alternative fuel to replace existing fuel options [6 - 8].

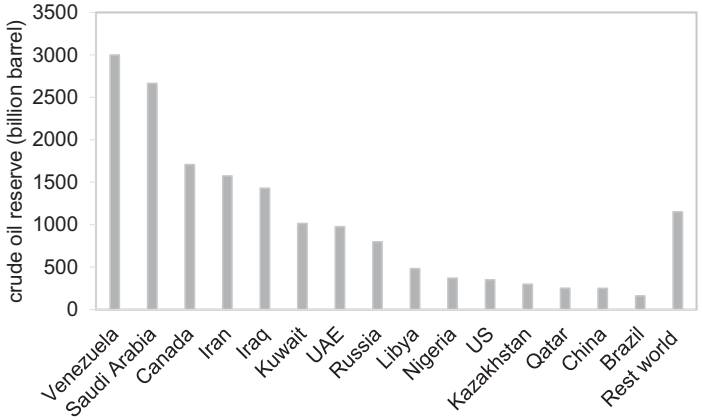

Fig. (1). Crude oil reserve status worldwide in 2020.

A blend of mono-alkyl-esters of long-chain fatty acids (FAME) is known as biodiesel, and it is obtained from sustainable stocks such as vegetable oil, animal fats, used/waste cooking oil, *etc*. The major benefits of biodiesel over petro-diesel are four-times biodegradability, non-toxic, sulfur-free emission, superior flash point, and no modification required in the existing engine [10 - 12]. Higher production cost is one significant limitation associated with bio-diesel for widespread commercialization of biodiesel [13 - 15].

Among the existing four biodiesel production processes, the transesterification of oil (triglycerides) is commonly accepted. Detailed mechanism of the transesterification process has been found in many open works of literature [9 - 15]. A multi-step process (esterification-transesterification) is required for biodiesel synthesis and increases the energy required for processing [16 - 20]. Intensified technologies based on microwave and ultrasound applications for

chemical processing have several advantages, especially energy requirements for biodiesel production. Heat and mass barriers in esterification and transesterification reactions require enormous energy and reaction time [15 - 20]. The most used homogeneous catalyzed biodiesel production process required more energy/time for downstream processing to separate the final product. Heterogenous catalyst processes are developed to address the shortfall associated with the homogenous catalyzed processes. Mass transfer limitation in heterogeneous phases requires higher processing time and energy [18 - 20]. Simultaneous microwave and ultrasound application is a promising innovation approach to address the shortcoming in heterogeneously catalyzed biodiesel synthesis. The dielectric effect of microwaves releases a large amount of energy to address the heat transfer issue [2 - 4]. The cavitational effect of ultrasound, such as particle fragmentation and molecular excitation, may overcome the mass limitations in the biodiesel synthesis process [6 - 8]. Simultaneous microwave and ultrasound applications can be performed by inserting the non-metallic ultrasonic probe in the microwave cavity to avoid the metal arc formation reactor [13 - 18]. Irradiation of the cavity is avoided by tightening the horn with metallic mesh. The first simultaneous application of microwave-ultrasound was done for hydrazinolysis of esters. The simultaneous application performance was compared with the impact of ultrasound/microwave/conventional methods. The reaction time was reduced from 9 hrs. to 40 seconds, with an increase in yield from 73 (conventional) to 84% (ultrasound-microwave). The performance for the simultaneous effect was much better than the effect of microwave/ultrasound when used alone [16]. The design of a microwave cavity for simultaneous application is one of the significant challenges for process engineers. Some of the commercial applications have been reported in sequential effects for microwave-assisted ultrasound processes [18 - 20]. However, more efforts are essential for the advancement of microwave-ultrasound technology for biodiesel synthesis. The chapter discussed the potential application of non-edible feedstock for biodiesel synthesis. A detailed discussion has been reported on the basic ultrasound, microwave, or simultaneous application of ultrasound and microwave effects.

POTENTIAL NON-EDIBLE FEEDSTOCK

Biodiesel synthesis from potential renewable stock material is necessary for depleting petroleum resources and greenhouse emissions from non-renewable feedstock [23 - 25]. Table **1** lists the potential non-edible feedstock in India. Many biodiesel plants are operational in India, and the cost of these plants depends on the availability of low-cost feedstock and continuous supply. Most operational plants used palm oil as feedstock which was mainly imported from Malaysia and Indonesia. It has potential application for edible purposes, and the cost of crude palm changes with the international market and may disturb the competitive cost

CHAPTER 8

Intensification of Biodiesel Production Process using Acoustic and Hydrodynamic Cavitation

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Abstract: Biodiesel is an alternative to conventional fossil fuels. It has several advantages over conventional fuels. It is non-toxic, renewable, and biodegradable with no sulfur content. Researchers have used different techniques to produce biodiesel from various edible and non-edible oil sources in the last many years, but these technologies have several disadvantages. They are highly energy-intensive, have high operating costs, low volume throughput, and require high investment costs that make them uneconomical for large-scale operations. In recent years, sonochemical reactors such as ultrasonication or acoustic cavitation (AC) and hydrodynamic cavitation (HC) have been considered promising, efficient, and environmentally acceptable techniques for synthesizing biodiesel. These techniques work on the principle of generation, growth, and collapse of cavities due to pressure variation within the solution. The cavity collapse releases a tremendous amount of energy within a short period, typically within a microsecond at multiple locations within the solution. The release of such immense power generates local hot spots and highly disruptive pressure shock waves, which help in increasing the mass transfer rate and thereby causing improved transesterification reactions.

This book chapter reviews the primary mechanism of intensified approaches using cavitation, fundamentals of acoustic and hydrodynamic cavitation reactors, basic designs, and operational guidelines for obtaining the maximum biodiesel yields. This chapter discusses the effect of various operating parameters of AC and HC on biodiesel yield. In the case of HC, details of different cavitating devices and the impact of geometrical and operating parameters that affect the cavitation conditions and biodiesel yield are discussed.

Keywords: Acoustic cavitation, Biodiesel, Cavitation, Hydrodynamic cavitation.

INTRODUCTION

Increasing energy consumption is causing the inevitable depletion of fossil fuels at an alarming rate. In the current scenario, it is necessary to search for an alterna-

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tive fuel to cater to the demand, which must be environmentally acceptable, economically competitive, and readily available [1]. The most important reason is the increasing demand for fossil fuels in different areas of human life, such as transportation of goods using vehicles, generation of power, various processes in industries, and residential consumption. The increased use of such conventional fossil fuels gives rise to many problems such as significant emission of CO_2, global warming, and emission of greenhouse gases. Such increased use of these conventional non-renewable fuels leads to the depletion of these fuels and may get exhausted within ten decades [2]. Biodiesel is one of the promising biofuels, which is non-toxic, renewable, and biodegradable with no sulfur content and can be easily blended with the existing fuels for its ready use in the current automobile engine [3]. It also decreases the discharge of the unburnt material in the form of CO, SO_2, hydrocarbons, and NO_x. It can be produced from both edible and non-edible oil sources depending upon the availability of feedstocks [4].

Researchers worldwide have been producing biodiesel from different oils, such as edible and non-edible sources of oil. There are many reports on the synthesis of biodiesel using edible oil. Still, the extensive use of edible oil can cause the lack of availability of edible oil for human nutrition. However, using non-edible oil or waste cooking oil reduces the overall cost of biodiesel and makes the process more economical. Whenever a process becomes economical, commercialization also becomes more manageable. Therefore, nowadays, due to more awareness among researchers regarding the crisis of edible oil for human nutrition, researchers have shifted towards using non-edible or waste cooking oil (WCO) to synthesize biodiesel [5 - 9].

A vast amount of WCO is getting produced worldwide, and oil dumping is one of the biggest problems for hotels and industries. The triglycerides present in the WCO contain a large amount of energy, and therefore WCO can be converted into various chemicals by carrying out chemical reactions such as transesterification. Researchers have used multiple processes such as oil pyrolysis, thermal cracking, emulsification, the blending of oil with diesel, and transesterification. The emulsification and thermal cracking techniques produce various unwanted side products like aliphatic or aromatic compounds. Also, these processes enhance the deposition of carbon and cause the thickening of the oil. Therefore, to overcome these drawbacks, transesterification of oil using alcohol and catalyst is the best process available for biodiesel synthesis [5]. This process has some advantages, such as recovering unreacted alcohol and catalyst.

When oil or fat reacts with alcohol in the presence of acid or base catalyst, the reaction is known as a transesterification reaction. It produces mono-alkyl esters of long-chain fatty acids or commonly known as biodiesel and glycerol as a by-

product. This glycerol can be further used to synthesize various value-added products. Ethanol and methanol are the most used alcohols for the synthesis of biodiesel. These alcohols are cheaper, environmentally friendly, and readily available in the market. The esters formed using these alcohols are known as fatty acid ethyl esters (FAEE) and fatty acid methyl esters (FAME) [10]. The entire mechanism of the reaction happens in a stepwise manner where diglycerides, mono-glycerides, fatty acid methyl esters, and glycerol occur. The quantity of all the products depends on the type of oil used, oil to alcohol molar ratio, catalyst type and amount, and overall process conditions [4]. The oils having a large amount of free fatty acid (FFA) content have very high acid value. This reduces the overall yield of biodiesel since FFA initiates the unwanted reactions of soap formation. The overall rate of transesterification reaction mechanism and biodiesel yield entirely depends on the quantity of unsaturated fatty acids present in the oil. The amount of saturated fatty acid decides the physical properties of the oil, such as cloud point, cetane number, *etc*. [3]. The transesterification reaction can be carried out in batch and continuous processes, but the continuous processes are more economical than batch processes [3, 11, 12]. The waste cooking oil or non-edible oil may contain a large amount of FFA. The transesterification of such oils is not feasible since higher FFA content may lead to soap formation instead of biodiesel in the presence of catalyst and alcohol. To avoid soap formation, a two-step process including acid esterification followed by alkali transesterification can be carried out for biodiesel production [2, 13].

The transesterification reaction depends on many factors such as oil to alcohol molar ratio, catalyst concentration, the temperature of the reaction, and the process parameters of the reactors. The catalysts required to carry out transesterification reactions can be divided into two types such as a homogeneous and heterogeneous catalysts. These catalysts can be further classified into two categories such as acid and alkali catalysts [3]. Conventionally, the transesterification reaction uses a homogeneous catalyst (acid or base) since it provides a higher reaction rate in biodiesel synthesis [14, 15]. But the separation of unreacted alcohol and catalyst is one of the most challenging and costly parts of this approach. Also, the final product obtained after the homogeneous transesterification process needs water washing to remove the unreacted traces of catalyst and alcohol. The water used for washing needs further purification, making this approach less feasible [16]. But, in the case of heterogeneous catalysts, separating unreacted catalysts and alcohol is easy, and the catalyst can also be reused after regeneration. Also, the water washing step can be avoided in heterogeneously catalyzed transesterification. The separation of biodiesel, glycerol and unreacted catalysts is easy due to three different phases.

CHAPTER 9

Improved Enhanced Oil Recovery – Role of Sonication: An Overview

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Abstract: Crude oil is one of the prominent resources to fulfill the need of day-to-day life. With few reservoirs, the proper utilization and maximization of oil recovery from existing oil wells are one of the foremost objectives in today's scenario. Conventionally, the inbuilt pressure and artificial pumping followed by water flooding could result in 30-50% of oil recovery. Thus, to produce the remaining residual crude oil, various enhanced oil recovery methods are adopted, including gas flooding, fire flooding, chemical EOR, *etc*. Still, oil recovery in large quantities persists to be a challenging task for engineers throughout the world. The major limitation for improving the oil recovery is the water enrichment of the reservoirs, which governs the oil displacement efficiency from the reservoir to the production platform.

The application of sound waves in reservoir engineering is an established technology. In seismic surveys, sound waves of various frequencies have been used to predict oil and gas reserves. The advancement of the application of ultrasound irradiation on multiple sectors, including the enhancement of oil recovery from wells, has also been analyzed and tested. The idea behind applying cavitation technology is that the passage of ultrasound waves releases the energy in terms of transient cavitation and allows the formation of the fine emulsion of two immiscible phases. The emulsion enables the improvement of oil movability toward the production well without changing the porosity and permeability of rocks. Thus, the cavitation technique can be applied to estimate oil-water saturation in reservoirs and can further improve the oil recovery factor. This chapter emphasizes the fundamentals of enhanced oil recovery schemes, their mechanisms, and the application of ultrasound irradiation toward improved oil recovery.

Keywords: Cavitation, Crude oil production, Enhanced oil recovery, Emulsion, Permeability, Surface tension.

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INTRODUCTION

The demand for petroleum-derived fuel and chemicals has increased tremendously over the past few decades and will remain in force for upcoming years. The fossil reservoirs are limited, and the total estimated oil reservoir is 1.66 trillion barrels globally [1]. In the current scenario, almost 70-80% of the reservoirs were explored, and with the current oil consumption rate, the reservoirs are estimated to supply oil for the coming 45-50 years [1, 2]. The limited resources of fossil fuels and unceasing increase in the demand required oil production from the reservoirs at the maximum level. Oil and gas recovery can be classified under three categories: primary, secondary, and tertiary or enhanced oil recovery (EOR). In the first phase of production, *i.e.*, primary oil recovery, the oil and gas are recovered through the displacement of oil and gas inside the reservoir by the inbuilt pressure of the fluid in the reservoir. Several mechanisms, such as solution-gas drive, gas cap expansion, water influx from aquifers, *etc*., through which this displacement can occur inside the reservoirs to provide the necessary energy to the hydrocarbons for their movement into the production well [3]. Once the available energy from the hydrocarbon is utilized, further recovery of hydrocarbons from the reservoir is carried out with the help of external pumping mechanisms such as a beam pumping unit (horsehead pump) or submersible pump [4]. However, this primary recovery is varied from reservoir to reservoir as the composition and reservoir conditions vary periodically [3, 4]. As soon as the associated water with the hydrocarbons exceeds more than 50%, the primary recovery ends, and the secondary recovery phase starts [3]. The secondary recovery, or the second phase of oil and gas production, allows the additional recovery of hydrocarbons either using water flooding or gas lifting (gas flooding) [4]. In both cases, the water or hydrocarbon gases produced through the production well can be again re-entered into the reservoir after separation. In case of water flooding, the produced water after treatment is allowed to enter through the injection well in a definite pattern such as a 5-point (1 production well surrounded by 4 injection wells) or 9-point pattern (1 production well surrounded by 8 injection wells). The injected water pushes the residual oil towards the production well, and based on the sweep efficiency, oil recovery is anticipated. In gas flooding, the gases are injected in the production tubing or in the reservoir depending on the oil and reservoir properties. In the overall scenario of hydrocarbon production from the reservoir, the rock properties such as porosity, permeability and wettability control the movement of oil, gas, and associated water [4, 5]. Thus, the combination of primary and secondary schemes will displace around 20-35% of the original oil-in-place and a huge fraction of the crude oil that stays entrapped in the reservoir will require special methodologies for production in an economical way [6].

To meet the demand across the world due to limited fossil resources, enhanced oil recovery plays an important role which involves all workable methodologies that can increase the oil production (as well as reduce the water production) beyond the primary and secondary oil recovery [3, 4]. The widely used workable tertiary recovery (or enhanced oil recovery) methods includes fire flooding, steam flooding, alkali flooding, surfactant flooding, polymer flooding, nanofluid flooding, and microbial flooding [7 - 12]. Together all the production methodologies can recover hydrocarbons ranging from 35 to 55% depending upon the nature of the hydrocarbons, reservoir, and the properties of rocks [3]. The details on various recovery mechanisms can also be found in the above-cited literature. The reservoir rock properties are the foremost essential parameters in any production field; hence, in subsequent sections, all these parameters have been discussed briefly.

Typically, the heavier hydrocarbons with API gravity from 17-28oAPI are highly viscous and possess poor displacement efficiency due to their lower wettability and permeability. Thus, enhanced oil recovery methods play a vital role in maximizing the production of such reservoir fluids [6]. The approach used in different methods for enhanced oil recovery mainly focuses on improving flow properties of hydrocarbons, *i.e.*, reduction in viscosity along with a decrease in oil saturation and wettability alteration of reservoir rocks. It causes the hydrocarbons to move through the interconnected pores toward the producing well [9]. Recently, a few researchers investigated the role of sonication in enhanced oil recovery. The primary approach is to form a stable emulsion of oil and water so that the two-phasic fluid becomes converted into a single phase and the flow of hydrocarbons can be improved [13]. In this chapter, the various technical parameters for the application of sonication in enhanced oil recovery have been discussed in detail.

IMPORTANT PROPERTIES OF RESERVOIR ROCK

During the drilling operations, the collected rock cuttings of the underground surface from an oil well are called core samples. These core samples are further analyzed in the lab to understand the various properties of the rocks and associated fluid. The core sample analysis provides all the necessary information for the reservoir and further allows performing various experiments to improve or alter the fundamental properties. Some of the most crucial properties are discussed as follows:

The Porosity of the Rock

The porosity of the reservoir rock is one of the crucial properties, which permits the flow of hydrocarbons and associated water from one point to another. The

CHAPTER 10

Role of Sonication in the Upgradation of Heavy Crude Oil

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Abstract: The increase in energy consumption throughout the globe with declining global light-oil reserves necessitates the utilization of heavy crude oil reservoirs to meet the demand. The processing of heavy crude oil in refineries creates extensive loads on thermal and catalytic processes to upgrade them as well as to meet market legislations. Heavy crude oil is rich in excess sulfur and other metals along with high molecular hydrocarbons such as resins, waxes, asphaltenes, heavy aromatics, *etc*. The separation of lighter hydrocarbon fractions is difficult as well as the processing of vacuum residue also needs attention. The thermal processes break the heavy hydrocarbons into smaller ones which later can be reformed or cracked using catalytic processes. The catalytic processes cannot be employed directly as the impurities will poison catalysts. Thermal processes such as vis-breaking, thermal cracking and coking are highly energy intensive processes and mainly progress through free radical mechanism. The application of ultrasound in the upgradation of heavy crude oil will help in the reduction of energy requirements and load on these thermal processes. The present chapter overviews ultrasound-assisted cavitation as an innovative method to intensify the cracking of asphaltenes and other heavy hydrocarbon molecules existing in the vacuum or atmospheric distillate residual.

Keywords: Catalytic process, Cavitation, Cracking, Heavy crude oil, Thermal process, Upgradation.

INTRODUCTION

The discovery, exploration and utilization of crude oil are the most essential contributors to the development of society over the last century. The chemical engineers have explored the various fractions of crude oil and further transformed them into different grades of fuel and petrochemicals. Nowadays, the dependency of society on petroleum products is extremely high and to meet the future demand

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with limited available petroleum reservoirs is a daunting scenario. Over the past few decades, the distributed combustion of petroleum based fuels through transport vehicles has expanded exponentially and causes environmental damage such as global warming and greenhouse gas effects. In order to minimize further environmental damage, the use of renewable fuels is geared up and an alternative fuel-based transportation system came up as a potential substitute to the conventional one [1]. But to replace the petroleum-based fuel economy to 100% renewable fuel based is not feasible and even reducing the global consumption of petroleum-derived fuel is also a major challenge in the current scenario [2]. The renewable fuel will definitely increase the share in coming years, but the dependency of society on petroleum will remain unaffected as the demand for petrochemicals and related products will surge exponentially in the coming years [2, 3]. The available reservoirs of crude oil (producing and explored) are now enrich with heavy hydrocarbons along with impurities such as sulfur, nitrogen, oxygen and rare earth metals [3, 4]. The competitiveness in reducing the environmental pollution and processing of heavy crude oil is the major task throughout the globe that refineries are facing [3, 6]. Thus, the development of newer technology to convert the heavy crude oil residue into the more valuable or lighter products in a cost and energy efficient way is one of the challenges to the researchers who are actively working in this area [7]. Typically, the crude oil at the end of fractionating (through the atmospheric and vacuum distillation) results in 30-60% of heavy fractions that need to be upgraded in the refinery [6, 7]. Fig. (**1**). shows the representative composition of lighter and heavier crude oil per barrel. It is anticipated that in the coming years, refineries will have to process heavy crude oil having densities > 25^{o}API [8]. Thus, the transformation of heavy residues into lighter products is one of the major loads in refineries. The conventional or ongoing upgradation process employed in the refinery includes thermal processes – visbreaking (mild cracking) and coking, as well as catalytic processes – catalytic cracking, catalytic reforming, hydrocracking, isomerization, *etc*. for up-gradation of heavy fractions of crude oil [6, 7, 9]. Among these several processes, cracking (either thermalor catalytic) is the typical process that breaks down the large hydrocarbon molecules into the smaller one, whereas reforming and isomerization are the catalytic processes that mainly transform the hydrocarbons into their isomers with minimum change in carbon numbers [6, 9]. In the next section, the brief working principle of these processes is discussed.

CONVENTIONAL PROCESSES FOR UPGRADING OF HEAVY CRUDE OIL

As stated in the previous section, the cracking (break down) of heavy or residual hydrocarbon molecules into the lighter or smaller ones is a must in the refinery operations to improve the overall economy of the refining processes and also, to

meet the market demand of the lighter-end hydrocarbons. Typically, the crude oil is a mixture of (more than 1000) hydrocarbons existing from C_1 to C_{70} [4]. The API gravity and the distillation characteristics will give the estimation of hydrocarbon composition of the crude oil [6]. The heavy residue which is also known as the bottom of the barrel is the fraction of crude oil which has a boiling point of > 400°C [10]. The crude oil is first desalted in the refinery to remove the salt and water impurities and then sent to the distillation column for further fractionation. The process will give several cuts (such as LPG, gasoline, kerosene, diesel, aviation fuel, *etc*.) based on the boiling points range and can be further blended/treated to meet the standard specifications [6, 8, 9]. In the overall process of separation of various fractions through the crude distillation column (through both atmospheric and vacuum), a precaution is taken that no breakdown of heavy hydrocarbon occurs in it, as it will create the operation instability due to a sudden change in the composition of hydrocarbon (and their pressure) as well as the deposition of residual carbon into the distillation columns [6]. The heavy fractions obtained from the vacuum distillation and the residue of the process have less demand in the market and thus their conversion into the lighter end products is more important [5, 7]. The various cracking processes used in the refinery for this purpose are explained briefly in this section as follows.

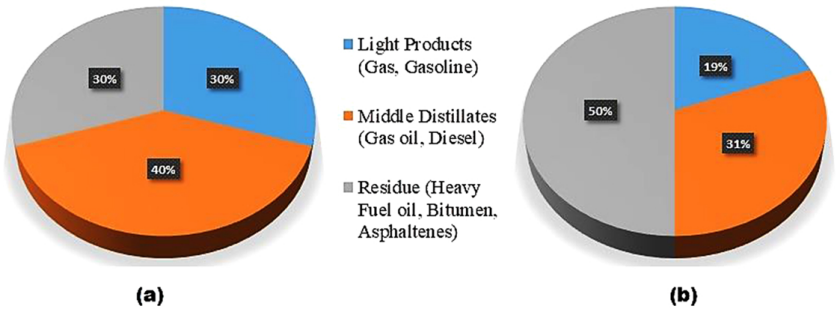

Fig. (1). Representative types of crude oil (**a**) light crude oil (44°API) and (**b**) heavy crude oil (31°API) (Adopted from Speight and Özüm [8])

Thermal Cracking Processes

The heavy hydrocarbon molecules are heat sensitive and easily broken down to the smaller ones when heated over 400°C. Conventionally thermal cracking processes are classified into two categories *viz*. 1. Visbreaking and 2. Coking. The visbreaking is also termed as mild cracking process in which the viscosity of the crude fraction is lowered down by breaking the long chain molecules into smaller ones [9, 11]. This unit is typically operated in between the temperature range of 440 to 490°C and a pressure between 50-200 PSIG to minimize the coke and gas formation. The conventional feed for this unit is the atmospheric residue or the

CHAPTER 11

Sono-Bio-Desulphurization of Liquid Fuel using Free and Immobilized Cell

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Abstract: In view of environmental concerns, the production of clean energy is one of the most critical issues in modern years to accommodate the growing energy needs of society (domestic usage), agriculture, and industry. Clean energy can be accomplished in several ways. A possible solution to this issue is to use renewable energy sources such as solar, wind, and nuclear power universally. The use of conventional techniques to produce energy by the combustion of fossil fuels has adverse effects on the environment due to the emission of greenhouse gas that contributes to global warming. The conventional method adopted by petroleum refinery industries has not been successful for profound desulphurization to achieve low sulphur contents. To overcome this, several new alternative chemicals, and physical and biological techniques have been developed to meet ultra-low sulphur fuel in the last two decades. Microbial desulphurization is one of the emerging alternative techniques that can remove the organo-sulphur compounds from fuels. The limitation of microbial desulphurization is the slow kinetics and it can be overcome by combining it with other desulphurization processes (hybrid system), such as the ultrasound-assisted processes. This chapter presents a critical account of research in different facets of ultrasound-assisted biodesulphurization. The microbial desulphurization process involves the use of free or immobilized microorganisms over the PU foams and the application of enzymes for desulphurization of DBT. The enzymes or proteins can act as catalysts to degrade sulphur compounds present in fuels. The present chapter also deals with the ultrasound-assisted microbial and enzymatic pathways. The concurrent analysis of experimental results on enzymatic biodesulphurizarion along with simulation results of cavitation bubble dynamics provides more insight into the actual mechanism of ultrasound on microbial and enzymatic desulphurization process.

Keywords: Cavitation, Hybrid desulphurization system, Immobilized cells, Microbial desulphurization, Ultrasound.

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INTRODUCTION

In recent years, the generation of clean energy has been the major concern to cater to the growing energy needs of the society (domestic usage), agriculture and industry. Energy production in an efficient manner can be achieved in several ways. A possible solution to address this issue is the use of renewable energy sources such as nuclear power, and solar, and wind which are being increasingly used worldwide. The conventional technique to produce energy by combustion of fossil fuels has adverse effects on the environment due to the emission of greenhouse gas that contributes to global warming. In addition, emissions of other gases such as SOx and NOx during the combustion of fossil fuels also cause colossal damage to the environment [1]. These generated gases are toxic in nature and react with water droplets in the atmosphere to cause acid rain. Acid rain can acidify the soil which ultimately leads to the removal of soil nutrients such as calcium and magnesium from the soil. It can also cause the loss of forests due to the weakening of trees' natural defense. In addition to that, acidification of other aquatic ecosystems such as lakes, rivers, and streams occurs which can cause enormous harm to fish and other aquatic life. Acid rain is also responsible for other destructive effects such as damage to the building materials and paints. SOx and NOx emissions during the combustion of fossil fuels are the consequence of the presence of contaminants in the fuel in the form of sulphur/nitrogen. The formed sulphur and nitrogen compound undergo oxidation to form SOx and NOx and these gases are emitted into the atmosphere. Several sulphur containing compounds witnessed in the form of thiols, sulfides, disulfides, and thiophene are originally present in crude oil. To curb the environmental pollution due to emissions of SOx and NOx through the vehicular exhaust, stringent guidelines have been enforced by several countries on the sulphur content of the fuel. The U.S. and Europe environmental regulatory agencies have restricted the maximum allowable sulphur emission to the environment from liquid transportation fuels, *viz*. diesel and petrol to 15 and 30 ppm, respectively.

Hydro-desulphurization (HDS) is the conventional method adopted by petroleum refineries by which the sulphur-containing compounds can be removed in terms of H_2S from the liquid fuel or crude oil.

However, HDS process is not suitable for hindered sulphur compounds due to its low reactivity and hence leads to reduce the removal rate [2]. In addition, hydrodesulphurization (HDS) also holds many other drawbacks. It operates under the extreme operating conditions and requires more expensive hydrogen in additional quantity. Due to these reasons, during the last two decades, several new alternative chemicals, physical and biological techniques were developed to meet ultra-low sulphur fuel. Microbial desulphurization is one of the emerging

alternative techniques that can remove organo-sulphur compounds from fuels. The limitation of microbial desulphurization is the slow kinetics, and it can be overcome by combining with other desulphurization processes (hybrid system), such as the oxidative desulphurization process or ultrasound-assisted processes, to produce Sulphur free liquid fuels. The microbial-assisted desulphurization reaction is mainly an L-L heterogeneous systems and this reaction is limited by mass transfer. This type of reaction kinetic mainly relies on the actual interfacial area available between the organic and aqueous phases. Sonication is a well-known tool to enhance the kinetic as well as the yield through strong convection generated in the reaction system that eventually leads to reducing the mass transfer limitation between the phases. This chapter aims to present more insight into the physical and chemical mechanism of the sono-hybrid processes *i.e*. the combinations of bio desulphurization treatment with ultrasound. These sono-hybrid systems have also been combined with various reaction conditions such as free and immobilized cells and different types of surfactants which help to enhance the transportation of microbes from aqueous to the oil phase.

Sulphur Compounds present in Liquid Fuels

Sulphur compounds in petroleum fractions are mostly derived from the decomposition of organic components. Generally, sulphur compounds have been found as hydrogen sulfide, whereas some quantities of sulphur compounds remain in liquid form in petroleum fractions. Apart from these, there is another possible theory to form sulphur compounds engaging reduction of sulfates in the presence of microbes. Furthermore, the formation of reservoir rock depends on the temperature, pressure, and time, *etc.* Sulphur is one of the ample compounds observed in the petroleum fraction. Sulphur concentrations in crude oil can vary from 0.4 to 14 weight percent depending on the origin and geographical source [2]. Generally, high-density crude oil has low API and high sulphur compounds. Therefore, the fractions of sulphur compounds distribute due to the boiling point of the distillate fraction. The sequence of sulphur concentration observed in several compounds as follow: saturates < aromatics < resins <asphaltenes [3].

Sulphur Problem

Heavy crude oil contains sulphur in concentrations ranging from 0.1% to 15% (w/w) [4]. Sulphur compound present in petroleum fraction is known to be an undesirable compound due to its harmful effect, and unfavourable influence on vehicular engines. Refractory organo-sulphur compounds in petroleum also lead to an increase in the viscosity making it non-acquiescent to the petroleum refinery process [5]. The sulphur is more corrosive in nature, and hence the possibility to corrode metallic parts involved in the process is more. The corrosive nature of

CHAPTER 12

Physical Insight into Ultra-low Desulfurization of Liquid Fuels using Sono-hybrid Fenton Reaction

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Abstract: The sulfur-containing hydrocarbons are the main source of SO_x and CO_2 gas emissions, which is a threat to the environment for sustainability development. According to the US environment protection agency, the sulfur content should be within the limit of 15 ppm and 30 ppm for diesel and gasoline, respectively. Also, a couple of advanced techniques have been developed so far for the removal of sulfur from fuels. Among these techniques, ultrasound-based advanced oxidation processes have been found to be more efficient and effective for sulfur removal.

In this chapter, we have discussed the physical and chemical mechanism of ultrasound based advanced oxidation processes including the influences of process parameters such as pH, the concentration of sulfur, concentration of oxidant, presence of phase transfer catalyst, oxalate ions, *etc.* Also, several hybrid techniques are discussed with their advantages and disadvantages for obtaining ultra-low sulfur fuel.

Keywords: Advanced oxidation processes, Cavitation, Desulfurization, Fenton, Ferrioxalate, Phase transfer catalyst, Photocatalysis, Reaction mechanism, Ultrasound.

INTRODUCTION

Climate change is the biggest crisis that the world is going through, but at the same time, the challenge is to maintain a constant energy supply for economic activities and growth. The dependency of human civilization on fossil fuels for the generation of energy is very old. Currently, 80% of global primary energy demand is being fulfilled by fossil fuels. This is also responsible for the rise in CO_2 emissions and other short-lived climate pollutants' (SLCP) emissions [1]. The reason for the shift from non-renewable sources like fossil fuel to renewable sources of energy like sun, wind, *etc.* is mainly due to the fact that fossil fuels are

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limited and are also the cause of environmental degradation. However, the intermittent nature of renewable energy resources is also a limit to which reliance on fossil fuels will remain.

The largest source of energy is crude oil. It is composed of various organic liquids, occurs naturally below the earth's surface and takes millions of years to form. Hydrocarbon products, *i.e*., diesel, jet fuel and gasoline are the major contributors to the transportation sector. The value of crude oil is measured through two properties, *viz*. its *American Petroleum Institute* (API) gravity value and the sulfur content value. Depending on the source and the type of crude oil, sulfur content is given as the percentage of sulfur by weight and it can be less than 0.1% to greater than 5% [2]. Sulfur compounds occur in different forms and can be divided into four major groups, *i.e*., sulfides, disulfides, thiophenes, and mercaptans. The inorganic sulfur constituents like elemental sulfur, pyrite (FeS_2), H_2S are readily removed from the feedstock. However, the disposal of organo-sulfur compounds is somewhat delicate. Regardless of the sources of energy (coal/crude oil), the raw materials for fuel invariably contain organo-sulfur compounds in various forms such as sulfides, disulfides, thiophenes and mercaptans in spite of the disparity in their amounts. Generally, the organo-sulfur compounds are conventionally eliminated in industries from the feedstocks by hydrodesulfurization (HDS) using Al_2O_3 supported Co-based ($CoMo/Al_2O_3$) and Ni-based catalysts ($NiMo/Al_2O_3$). The reason for the desulfurization process is to prevent corrosion issues during the refining process in pumping and pipelines. The other adverse effect of untreated sulfur in fuels is the release of toxic SO_x gases. These gases tend to react with the atmospheric water resulting in acid rain which not only impacts the whole ecosystem by acidifying the soil but also affects the buildings and automotive paint finishes. Moreover, several health issues like heart issues, respiratory illnesses, and asthma are also caused by sulfur emissions including the formation of atmospheric particulates. The presence of sulfur compounds in automobile fuels has a great impact on the efficiency of catalytic conversion reaction kinetics [2, 3].

At present, several technologies have been developed for desulfurization as shown in Fig. (**1**). The most studied processes for desulfurization are: (i) *hydrodesulfurization* (HDS), (ii) *adsorptive desulfurization* (ADS),(iii) *extractive desulfurization*(EDS), (iv) *biodesulfurization* (BDS), and (v) *oxidative desulfurization* (ODS) [4]. Hydrodesulfurization or hydro-treatment technique is the most popular technique that is being employed for the elimination of sulfur compounds in industries. In this process, heteroatoms like S, N, or O are modified into another chemical form by treating the fuel in a hydrogen stream. The main limitation of this process is that it is inefficient for the elimination of organo-sulfur compounds like thiophenes. Also, it is a very energy-intensive process and

operates under extreme conditions of pressures (>3 MPa) and temperature (>600 K) which is not very economical for any industry [5].

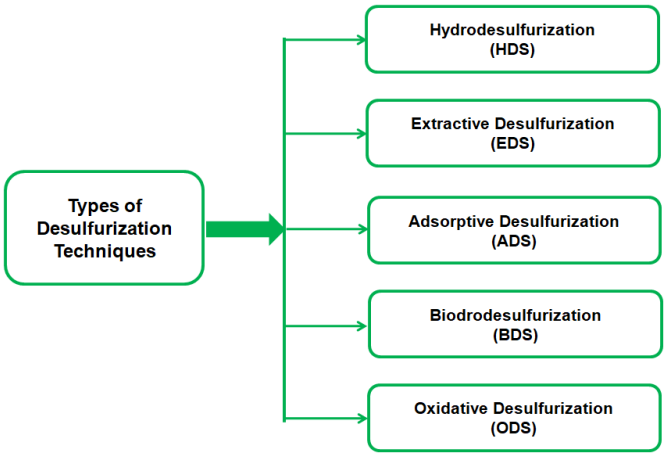

Fig. (1). Different types of desulfurization techniques based on their operation.

The *extractive desulfurization* is a liquid-liquid extraction technique that involves an extractant to dissolve the sulfur compounds from the oil. Some of the common extractants are pyrrolidone, N, N-dimethyl formamide, acetonitrile, and dimethylsulfoxide. In this process, the gravitational force is used for the separation of sulfur from the layer. The main limitation of this process is that these conventional extractants are very volatile in nature and are toxic which may have an adverse effect when applied in a large-scale separation [6].

Adsorptive desulfurization is comparatively a new technology that is based on the principle of physicochemical adsorption for the elimination of organic sulfur compounds from petroleum fractions. This method does not require any hydrogen and works under low pressure and temperature. The efficacy of adsorptive desulfurization is the function of the adsorbent's textural properties like high stability, more pore volume and surface area, mesoporous with decent surface-active sites, and good structural strength. However, this technique also suffers due to some limitations like reusability or adsorbent regeneration, mass transfer limitation affecting the selectivity in the real feedstock, and loss of mechanical strength at an elevated temperature [7].

The biodesulfurization is an alternate technology that is used in combination with the *hydrodesulfurization* process. This process is based on biological activity where strains of microorganisms, mainly bacteria are employed for the elimination of sulfur atoms from the fuel without hampering the carbon structure of the organo-sulfur compounds in the fuel. It is an environmentally friendly

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