A Brief Review on the Application of Ultrasonic Technique in Biodiesel Production

Basir Maleki ⬤**, Mohsen Mansouri** *⬤

1. Department of Chemical Engineering, Faculty of Engineering, Ilam University, Ilam, Iran. E-mail: b.maleki@ilam.ac.ir
2. Department of Chemical Engineering, Faculty of Engineering, Ilam University, Ilam, Iran. E-mail: m.mansouri@ilam.ac.ir

ARTICLE INFO	ABSTRACT
	The increasing pollution levels, rising energy demand, and the inadequacy of conventional fuels have spurred interest in alternative sources of fossil fuel supply and demand. This problem has shifted the focus towards the examination of a promising sustainable alternative for diesel fuels. In this sense, biodiesel can be a more suitable candidate for energy, environmentally harmless, and cost-competitive approach to respond to the energy demand. The application of ultrasonic energy in biodiesel production via transesterification has been endorsed as an efficient approach that improves mass transfer factors resulting in decreased reaction times and potentially lower process expense. This study investigates the advancements in ultrasonic energy for biodiesel generation from various raw materials utilizing different catalysts. A critical assessment of the current approach is furnished, emphasizing the application of ultrasonic irradiation. Besides, in order to better understand ultrasonic energy, each ultrasonic cavitation (UC) and hydrodynamic cavitation (HC) is discussed. Regarding each approach, the fundamental concepts are discussed in detail. Generally, the present study aims at conveying a comprehensive overview of ultrasonic energy usage in transesterification reactions and furnishing an outlook on prospective developments in the technology.

Introduction

Sustainable expansion in mechanization and transportation has remarkably raised the application of non-renewable fuels. Accordingly, it leads to a great emission of harmful and toxic gases into the ecosystem [1]. Environmental limitations are a critical aspect to motivate researchers to explore renewable and clean fuels. Biodiesel is an alternative fuel that offers a strategy to replace conventional diesel. Biodiesel can be straightly employed in a diesel engine without any changes owing to its resemblance attributes to diesel fuel, such as heat of combustion and density [2]. Moreover, biodiesel assists in environmental conservation because of its sustainable, biodegradable, renewable, and non-toxic nature, and also its capability to diminish CO, CO_2, and SO_x emissions [3]. Fuel yield and feedstock expense are the significant parameters that cause the biodiesel generation cost to become high. The transesterification process fundamentally incorporates the reaction between alcohol and triglyceride in the attendance of catalysts. Essentially, alcohol and triglyceride which are insoluble fluids form

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segregate phases in the blend [4, 5]. Accordingly, the conventional biodiesel production process needs a continued blending of the immiscible liquids for a long duration significantly to enhance the chemical reactions between the triglyceride and alcohol. This is due to the fact that biodiesel production process takes place only in the interfacial area of the two phases [6]. One of the challenges encountered in biodiesel production is to improve the mass transfer rate between triglycerides and methanol while minimizing costs. This involves some specific considerations such as feedstock expenses, energy utilization, time efficiency, and overall cost increment [4, 7]. The ultrasonic energy results in triglyceride and alcohol emulsion that supplies considerable surface areas for transesterification to take place [8]. Hence, it is commonly regarded that the reaction time is notably diminished [9]. Moreover, it has been confirmed that the ultrasonic approach is an efficient and applicable technique to enhance the reaction rates in the chemical process. In addition, considerable progress in the conversion and purity was also achieved to alter the process routes, or begin the processes in chemical and electrochemical systems [10]. Ultrasound, like other acoustic waves, causes periodic contraction and expansion of the molecular spacing within the mixture. This phenomenon results in the release and occurrence of compression and rarefaction processes, forming a sequence of molecular interactions. In this regard, when a considerable negative pressure gradient is applied to the fluid, the space between the molecules expands above the critical molecular length, which is essential to maintain the fluid intact. Furthermore, the fluid will disintegrate and cavities will be formed, which are described as cavitation bubbles [11]. Notably, ultrasonic energy furnishes mechanical energy for blending and also facilitates the necessary activation energy to begin the transesterification process. It has been noticed that ultrasonication improves the performance of the transesterification of animal fats and vegetable oils into biodiesel and, furthermore, enhances the rate of the process [12, 13]. Ultrasonic energy such as ultrasonic cavitation (UC) and hydrodynamic cavitation are efficient intensification approaches to prevail the mass-transfer resistance between reactant phases (triglyceride and methanol) leading to quicker reaction time and high biodiesel purity [14].

The review of previous research shows that a wide variety of studies has been conducted in the field of biodiesel production at the presence of various catalysts. Nevertheless, the studies that explore transesterification under ultrasonic irradiation are insufficient. In this regard, this study is directed toward the current progress in the development of ultrasonic energy employed to produce biodiesel from various sources of raw materials. This paper also highlights various types of cavitation originated from acoustic and hydrodynamic sources. Significantly, specific attention is being given to the transesterification reaction applying ultrasonic energy. Furthermore, three comprehensible tables combining diverse catalysts and feedstocks along with optimized reaction parameters are given to have a perspective of the recent strategies of biodiesel generation.

Ultrasonic Cavitation

The sound in the audible spectrum has no impact on various processes. Moreover, the standard frequency of sound that is audible by human is from 0.016 to 18kHz. Ultrasound is expressed as sound with a frequency exceeding the person's audibility range, that is, more than 18 kHz [14]. It is classified according to its frequency into a high frequency (1000–10,000kHz) with low power, which is normally utilized for diagnostic objectives and chemical investigation, and low frequency (20–100kHz) with high power employed for plastic welding and chemical process [15]. There are four kinds of cavitation, that is, hydrodynamic, acoustic, optic, and particle-induced. Cavitation was speculated by Leonhard Euler in the year 1754 [16]. It is the generation, development, and destruction of bubbles within a liquid and also radiating

a great quantity of energy over a slight zone. Moreover, it leads to a very high viscosity with severe agitation of liquid influences, creating a local hot spot and free radical formation [17]. In this sense, several theories have been proposed to explain how energy is released in cavitation, the most comprehensible of which in terms of quality is the hot spot theory [16, 17]. In this theory, assuming that the cavitation process is adiabatic, the temperature inside the bubble increases to about 730^0C during the collapse, and it can be calculated based on the size, temperature and pressure of the bubbles in the acoustic field. In this case, the acute conditions created by the cavitation process led to the thermal separation of liquid vapor, the production of high-pressure pulses and shock waves. Each bubble acts as an independent microreactor that creates sudden high temperatures of several thousand degrees and pressures of over a thousand atmospheres in an aqueous medium [14-17]. Cavitation has risen to prominence in chemical processing because of its capability to produce high temperatures and pressures under approximately ambient circumstances. The principal influence of ultrasound on various processes is the generation and destruction of bubbles and also raising the local temperature and pressure through releasing massive energy in the turbulence surge form. Moreover, this would affect the molecules to form high energetic radical kinds of biodiesel generation. High severity of shock produced by fluctuating the cavities with a vast contact area in the sono-reactor is remarkably efficient to eradicate the mass-transfer resistance during the process [15-19].

Low frequency is generally applied in generating biodiesel because of the prevailing physical impacts. Nevertheless, biodiesel purity decreases when more than 40kHz is employed. Furthermore, the ultrasonic power can be handled owing to the soap creation in rapid reaction [20, 21]. High frequency is not utilized for transesterification because the destruction of the cavity is more powerless than the oil and alcohol collision. A low frequency of ultrasonic irradiation would force, stretch/constrict, and squeeze the molecular distance of a mingled reaction which leads to pressure alteration. Afterwards, the reactant molecules will be continually shaken to produce an enormous number of microbubbles [22]. As a result, the cavities will expand further due to the significant damage incurred when they reach a specific threshold. Additionally, this asymmetric destruction of cavities produces turbulent flow, which disconnects the phase boundary. These micro-turbulences from the collision of liquid into another liquid can be approximated to a velocity of 180 m/s, forming efficient bending of the insoluble phases at their border and, then, resulting in emulsification [23]. This formation of emulsion resumes improving the interfacial area and mass transfer between the insoluble phases. Furthermore, the abrupt destruction of a bubble leads to a rise in the local temperature, enhancing the intimate cordial or interfacial area of insoluble phases and elevated pressure and, consequently, conducting the transesterification reaction in a low time [24]. The last stage is the formation of free radicals such as $OH^{\bullet}$, $HO_2^{\bullet}$, and $H^{\bullet}$ from the breakdown of solvent vapor ensnared in the cavitation bubble during a transient drastic destruction of a microbubble. In this regard, it can eradicate exterior blending and heating because of the generation of micro turbulences and local temperature. Due to cavitation bubbles, ultrasonic energy can improve the mass transfer within the sono-reactor and, therefore, raise the transesterification reaction rate [20-25]. Accordingly, it can diminish the operational expense and energy utilization because it needs less triglyceride to alcohol molar ratio, catalyst dosage, electricity utilization, and quicker time in phase detachment as compared to the mechanical stirring technique [26]. Usually, cavitation is divided into two types, transient and stable. Transient cavities generally do not last more than a few cycles, during which the cavities reach at least twice their initial radius in a few microseconds before violently exploding. On the contrary, stable cavities nonlinearly fluctuate around their equilibrium size with a lifetime of tens of cycles. At one time, it was thought that the amazing effects caused by cavitation were entirely due to the collapse of transient cavities. It is now believed that the fluctuation of stable bubbles is responsible for a significant share of the overall sonochemical effects [27].

The earliest studies on the application of ultrasonic irradiation in transesterification have been accomplished by Stavarache, Vinatoru, Nishimura, and Maeda [21, 26]. They assessed the biodiesel generation via transesterification process of vegetable oil at the presence of sodium hydroxide under ultrasound irradiation of 28 and 40 kHz. It was discovered that, via employing ultrasonication, the processing time was much quicker (0.5 h) to acquire 98% purity at both frequencies as compared to mechanical stirring which only gets 80% purity in 1 h under identical circumstances. In this regard, Maleki et al. [28] examined biodiesel production from canola oil at the presence of heterogeneous alkaline catalysts ($\alpha Fe_2O_3/ZnO$) while applying ultrasonic irradiation. They investigated the impact of ultrasonic time, the molar ratio of alcohol to canola oil, the catalyst concentration, and ultrasonic power while putting the ultrasonic irradiation at 20 kHz and ultrasonic amplitude at 50%. When optimum conditions i.e. ultrasonic time (29.22 min), ultrasonic power (278.46 W), methanol to canola oil molar ratio (11.25:1 mol/mol) and catalyst dosage (3 wt.%) were acquired, maximum yield increased to 94.21%. The results showed that ultrasonic irradiation can enhance the purity of biodiesel by 38.65% as compared to a mechanical stirring. Besides, Korkut et al. [29] investigated the experimental optimization of biodiesel production through ultrasonication (120 kHz) at the presence of heterogeneous catalysts. After optimizing and obtaining regression models from the D-optimal design method, the maximum efficiency of biodiesel for calcium oxide, dolomite and CaDG catalysts was acquired (98.7%, 95.9%, and 86.3%), respectively. The maximum yield of biodiesel (99.4%) was achieved under the conditions of catalyst dosage of 35.5% by weight, the molar ratio of methanol to oil of 8.47: 1 mol: mol, ultrasonic power of 40 W, time of 150 min, and reaction temperature of 60°C for CaO catalyst. Furthermore, Jookjantra et al. [30] scrutinized the optimization of the transesterification reaction of biodiesel derived from refined palm oil at the presence of CaO catalyst with ultrasonic waves under vacuum conditions. The operating parameters were designed using the response surface methodology (RSM) the results of which demonstrated that the highest experimental yield (96.12%) was achieved under the optimal conditions of 9.69:1 molar ratio, 8.77% by weight of the catalyst, 4.6 W/g ultrasonic intensity, and ultrasonic time 43.03 min. It is worth mentioning that Mootabadi et al. [31] explored the production of biodiesel from palm oil at the presence of heterogeneous catalysts of alkaline metal oxides (such as CaO, SrO, and BaO) with the asset of ultrasonication energy. They scrutinized the effect of ultrasonic time, the molar ratio of alcohol to palm oil, the concentration of catalysts, and varying the amplitudes of ultrasonic waves while setting the ultrasonic irradiation at 20 kHz and 200 W. Considering the obtained optimal circumstances, the maximum yield increased to 95% after 60 min of reaction time. The results illustrated that ultrasonic irradiation can improve the yield of biodiesel by 30-40% as compared to a mechanical stirring. Moreover, Goh et al. [32] studied the impact of consumed coffee oil to methanol molar ratio (1:10–1:60), catalyst dosage (0.5–4.5 wt. %), ultrasonic time (0.5–5h) and ultrasonic amplitude (20%–40%) on biodiesel purity without utilizing an external heating instrument because of the successive squeeze. Almost 97.11% of purity with a 1:30 molar ratio, 4wt.% of KOH, and 30% ultrasonic amplitude was attained via ultrasonic time for 3h. Additionally, Asif et al. [33] scrutinized the production of biodiesel from Salvadora alii oil and Thespesia populneoides oil through ultrasonic energy with a frequency of 20 kHz and a pulse pattern of 30 to 70% at the presence of SO_4^{-2} / SnO_2-SiO_2 catalyst. They showed that under optimal conditions, including ultrasonic irradiation time of 50 min, the ultrasonic amplitude of 50%, catalyst concentration of 3.5 wt.% and the alcohol to oil molar ratio of 13:1 mol: mol, the highest yield of 88% was achieved. In this sense, they concluded that pulsed ultrasonic irradiation is nearly three times more effective than mechanical stirring. In another study, Asif et al. [34] deeply investigated the production of biodiesel from Pistaciakhinjuk seed oil with a pulse pattern of 10s on / 3s off and a frequency of 20 kHz using ultrasonic technique.

Considering Pistaciakhinjuk seed oil, the highest biodiesel yield (92%) was achieved under optimal conditions of 1:10 molar ratio of alcohol to oil, catalyst dosage 3 wt.%, ultrasonic amplitude 50%, and ultrasonic time 30 min. Furthermore, regarding the optimal conditions for biodiesel from fig, alcohol to oil molar ratio 1:6 mol: mol, catalyst amount 3.5 wt.%, amplitude 45% and ultrasonic time 30 min, the highest yield was 88.60%. They indicated that ultrasonic waves decrease the reaction time by 70% as compared to the mechanical stirring method. Table 1 summarizes the studies on biodiesel production at the presence of various catalysts using ultrasonic irradiation.

Table 1. UC-assisted transesterification

Catalyst Type	Oil	C (wt.%)	A/O (mol:mol)	Time (min)	Ultrasound Factors	Yield (%)	Ref.
EFB-KOH	Treated Rubber Seed	15	15:1	30	500 W, 20 kHz	88	[35]
γ-Alumina	Karanja	1	9:1	35	120 W, 20 kHz	69.3	[36]
NaOH	Fish	0.5	9:1	2	500 W, 20 kHz	82.02	[37]
Sodium Methoxide	Aegle Marmelos Correa	1.3	9:1	1.4	315 W, 20 kHz	98.01	[38]
KOH	Food waste	1.28	6.08:1	20	700 W, 20 kHz	93.23	[39]
HPA/AC	Jatropha	3.5	25:1	40	240 W, 20 kHz	91	[40]
Eggshell-derived CaO	Palm	8	9:1	60	120 W, 20 kHz	92.7	[41]
KOH	Treated Waste Fish	1	6:1	30	400 W, 20 kHz	79.86	[42]
KOH	Palm	1	6:1	20	400 W, 24 kHz	93.84	[43]
K_3PO_4	Waste cooking	3	6:1	90	375 W, 22 kHz	92	[44]
SrO	Canola	2.5	9:1	30.7	130 W, 20 kHz	97	[45]
KCH_3O	Waste cooking	1	12:1	30	450 W, 22 kHz	90	[46]

Besides, Fig. 1 depicts a picture of UC reactor or sono-reactor.
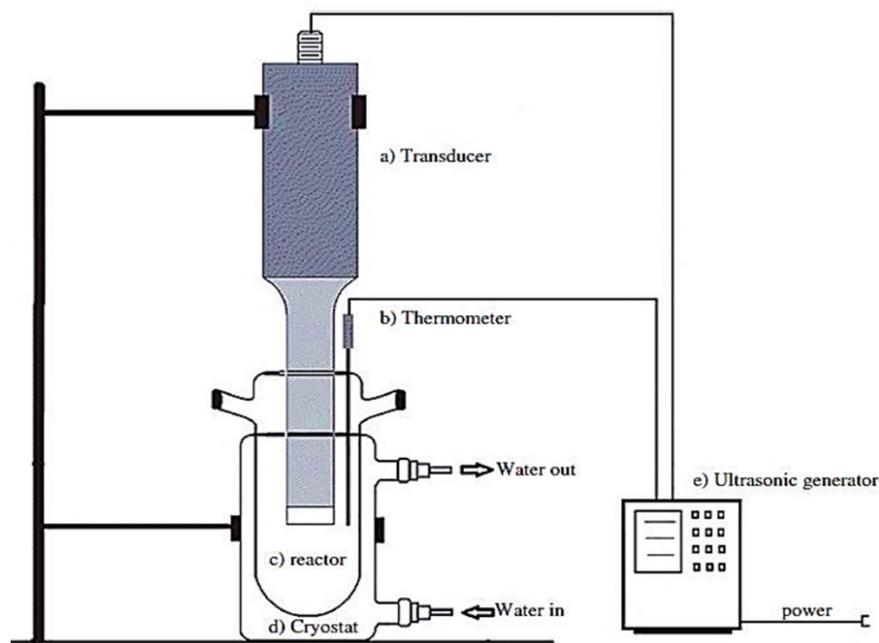
Fig. 1. UC reactor setup for transesterification reaction [46]

Mechanism of Intensification of Chemical Reaction based on Cavitation

In order to understand how cavitation affects chemical processes, it is necessary to pay attention to the possible effects of these bubbles in different systems. Regarding homogeneous liquid phase reactions, there are two main effects [43, 45]. The first effect is related to the

bubbles that are formed. These bubbles are not similar to a closed hollow container but are approximately filled with vapor, liquid or gases related to the solution. During the collapse of the bubbles, the release of these gases greatly increases the temperature and pressure, causing the breakdown of molecules and the formation of active radicals [46]. These radicals may react inside the bubbles or after the collapse of the bubbles or their transfer into the environment. The second effect is related to the sudden collapse of the bubbles, which causes the accumulation of the vacuum and, as a result, creates shear forces in the surrounding liquid. Moreover, it is capable of destroying the components of chemical substances or any soluble substances inside the liquid, as well as disrupting the layer. Significantly, it is worth mentioning that it is a borderline phenomenon. According to the reaction conditions in a cavitation process, the choices of solvent and temperature are important and influential factors. Any increase in the solvent vapor pressure results in a decrease in the pressure and maximum temperature in the bubble collapse [47]. The mechanical effect of using cavitation in a heterogeneous system is mainly the reaction activation. In heterogeneous liquid-solid systems, the collapse of cavitation bubbles leads to structural and mechanical changes. The collapse of bubbles near a solid surface causes the formation of a rapid flow of liquid on its surface [48]. Due to the existence of these fast and high-pressure liquid flows, ultrasound is used to clean solid surfaces. These liquid flows activate the solid catalyst and increase the mass transfer via disrupting the boundary layer between the two phases. The collapse of bubbles on a solid surface, especially powders, provides the necessary energy to crush materials. Therefore, in such a case, ultrasound increases the contact surface and causes the reaction to intensify through mixing and mass transfer more effectively [49]. Regarding heterogeneous reactions, there must be a balance between cavitation intensity and catalyst activity. Considering heterogeneous liquid-liquid reactions, the collapse of bubbles near the interface of the phases causes stirring, mixing and, as a result, the formation of an emulsion of the very fine particles. After the formation of the emulsion, the level of reaction between the two phases increases and, as a result, the reaction speed increases. Notably, the emulsion produced by cavitation has a smaller and more stable particle size than the emulsions produced by mechanical stirring [46- 50]. This type of emulsion is very useful in catalytic reactions that have phase transition or two-phase systems. A schematic of cavitation bubble and its associated effects is depicted in Fig 2.
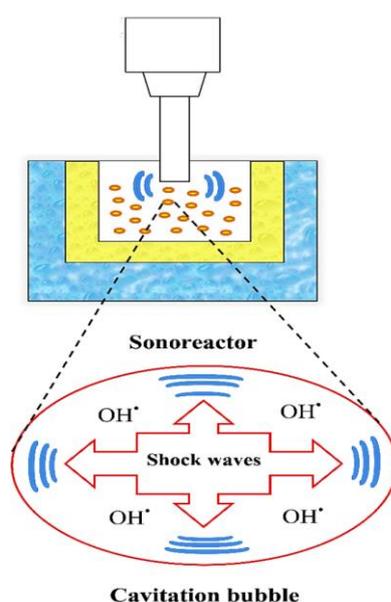
Fig. 2. A schematic of UC bubble

Parameters Affecting the UC

Since cavitation is the basis of sonochemical reactions, it is important to study factors affecting cavitation. By comprehending these parameters, it is easier to optimize the experimental conditions to have maximum sonochemical effects.

Frequency

Generally, there is no significant difference in the formation of cavitation bubbles at low-range frequencies (i.e., from 20 to 40 kHz). However, the time to complete the transesterification reaction is shorter when using a frequency of 40 kHz and a low catalyst concentration [50]. The reason is due to the faster formation of higher amount of soap (phase transfer catalyst). Definitely, in the separation stage, these soaps trap some ester molecules and reduce the overall efficiency of biodiesel production. As the frequency increases, cavitation in liquids decreases and, therefore, in order to achieve the same cavitation, the ultrasonic power must be increased [51]. At frequencies higher than 100 kHz, cavitation is not strong enough to cause two liquid phases to collide with each other. The mixing between the immiscible bilayer (alcohol and triglyceride) is very weak and, accordingly, the transesterification reaction occurs only at the boundary of the bilayer. Therefore, the use of low-frequency ultrasound energy is preferred for biodiesel production [52]. On the other hand, the frequency of ultrasonic waves affects the critical size of the bubbles. Moreover, increasing the frequency leads to a decrease in the volume and time of the collapse of the cavitation bubbles. It is worth mentioning that higher frequencies cause transmission activities at the boundary surface of the bubble. Therefore, emulsification is improved and the reaction speed of biodiesel production increases. Besides, the reduction of bubble collapse time due to the limitation of energy exchange with the environment acts like an adiabatic process. Regarding further increase in the frequency, the resonance of the bubble size is not large enough to provide the necessary energy for emulsification and, accordingly, increase the reaction rate. When the frequency increases, the expansion phase is shortened and, consequently, it is necessary to enhance the radiation amplitude to keep the balanced cavitation energy in the system [49-53]. In other words, when cavitation effects are kept constant, we need more power at a higher frequency. Moreover, when the frequency reaches the megahertz range, it becomes more difficult to create cavities in liquids. The simplest qualitative explanation of this problem is that at a very high frequency, the expansion (contraction) cycle is extremely shortened [54]. Notably, cavity production in the liquid is done through separating the molecules from each other at a certain time; thus, when the expansion cycle time is shortened from the above time, cavitation becomes difficult and impossible. Another important factor is that transducers, operating at these high frequencies, do not have the ability to mechanically produce a very high ultrasonic range [53, 54]. The frequency for activities like cleaning, plastic welding, and sonochemistry is typically chosen based on these factors, with a general range of 02 to 52 kHz.

Intensity

The intensity of the applied acoustic is directly proportional to the square of the vibration amplitude of the ultrasound source. Generally, any increase in radiation intensity causes more ultrasonication effects; but there are limits on the amount of ultrasonic energy that enters the system. In order to reach the cavitation threshold, a minimum intensity of sound application is needed [54], whose value depends on the frequency. Regarding high ultrasonic power use, numerous bubbles are created in the mixture, many of which create the formation of larger and longer-lived bubbles via merging with each other. Finally, like a barrier, they prevent the passage of acoustic energy into the solution [55]. Besides, at high vibration amplitude, the ultrasonic source can no longer stay in contact with the liquid through a complete cycle. Technically, this phenomenon which is called release causes the loss of large amounts of power

transfer efficiency from the source to the environment. Certainly, the *release* is mostly related to the cavitation bubbles that are formed in the vicinity of the bubble-forming part [56].

Viscosity

Negative pressure is required for the creation of bubbles within a liquid, causing molecules to be pushed apart from one another. The formation and collapse of bubble spaces inside the liquid create shear forces and, since viscosity is a measure of the fluid's resistance to these forces, cavitation is more difficult in a viscous liquid [57].

Surface Tension

The requirement for cavitation is to create a gas-liquid interface. When a solvent with a low surface energy per unit area is used, the cavitation threshold also decreases. However, adding surfactants to aqueous solutions facilitates cavitation [58].

Vapor Pressure

There are no voids for the cavitation bubbles. During phase expansion in cavitation bubble generation, vapor from the surrounding liquid penetrates into the interface. This action creates a small pressure inside the cavity, which reduces the pressure difference between the cavity and the liquid [59]. Cavitation is difficult in a solvent with low vapor pressure because less vapor enters the cavity. In highly volatile solvents, cavitation occurs with less acoustic energy and, accordingly, vapor is available to fill the bubbles. On the other hand, sonochemical effects are based on the energy released by the collapse of bubbles, which is reduced at the presence of vapor inside the cavity. Therefore, solvents with high vapor pressure easily create cavities and, thus, vapor fills the bubbles. But, at the same time, their decay is easier and, as a result, they release less energy [60].

Temperature

An increase in temperature leads to an increase in the vapor pressure of the substance and, therefore, facilitates the cavitation phenomenon. On the other hand, it weakens the collapse of cavities due to the reduction of viscosity and surface tension. Although at higher temperatures and near the boiling point of the solvent more cavitation bubbles are simultaneously formed, the effective ultrasonic energy of the source entering the liquid dramatically decreases due to the fact that these bubbles are like a barrier against the passage of acoustic [61].

Hydrodynamic Cavitation (HC)

HC is generally classified into two types of algorithms: inertial and non-inertial cavitation. Inertial cavitation is the procedure where the microbubbles destruct because of recuperation of pressure and release of a significant quantity of local temperature in the form of shock spirals. Therefore, enhancing local temperature and pressure in microseconds results in molecule breakdown and produces highly energetic radical types [62]. The reaction accelerates within the cavitation bubbles owing to the enhancing number of vigorous impingements within the fluctuating bubbles, which would be identical to supercritical circumstances. This demeanor can eradicate the mass transfer restrictions amongst two immiscible reactants in the reaction medium. Notably, it can be simply performed utilizing control valves [63]. Moreover, HC is known as a phenomenon in which microbubbles are formed because of the pressure drop through the passage of liquid via a constricted geometry including orifice and venturi. Based

on Bernoulli's formula, incondensable fluid streams via compression/geometry, whose speed enhances against the decrease in pressure [64]. The cavitation is formed through the generation of microbubbles whenever the fluid-flow via a relatively low-pressure area is under the vapor pressure of the current fluid. Afterwards, microbubbles asymmetrically disrupt when these bubbles stretch to the highest dimension below the isothermal circumstances as pressure recuperates downstream from the mechanical compression [62, 64]. The pressure recuperation shape in the downstream section of the orifice is considered to be linear. The impulsive destruction of these microbubbles is due to the recovery of pressure that discharges a remarkable quantity of local energy. In addition, it results in intensifying the local temperature and pressure which speeds up the process [65]. Non-inertial cavitation is the procedure in which a bubble in a liquid is compelled to fluctuate in dimension or form owing to the energy input, including an acoustic field. Non-inertial cavitation is frequently applied in ultrasound cleaning baths [64]. Regarding HC parameters, the quantity of cavitation is the most important factor that shows the movements related to HC based on the conditions of bubble formation and destruction. [63, 65].

Table 2 demonstrates the different investigations that have been documented in biodiesel production achieved from various raw materials utilizing HC techniques [66].

Table 2. HC-assisted transesterification

Catalyst	Oil	Molar Ratio (mol:mol)	Catalyst Dosage (wt.%)	Time (min)	Ultrasound Factors	Yield (%)	Ref.
KOH	Frying	6:1	1	10	7.5 kW	95	[66]
KOH	Nagchampa	6:1	1	20	1.5 kW	92.1	[67]
CH3OK	Waste Cooking	12:1	1	30	450 W, 22 kHz	82.9	[68]
KOH	Waste Cooking	6:1	1	15	4 kW 2 bar	97	[69]
KOH	Treated Rubber Seed	6:1	1	18	4 kW3 bar	97	[70]
NaOH	Waste Cooking	6.8:1	1	5	1.1 kW, 7 bar	99	[71]
KOH	Frying	4.5:1	0.55	20	1.75 kW, 3 bar	93.6	[72]
KOH	Frying	6:1	1.1	8	3.27 bar	95.6	[73]
KOH	Rubber Seed	6:1	4.5	40	0.373kW	92.5	[74]
KOH	Schleichera Oleosa	6:1	0.75	30	2.2 kW	95	[75]
TiO_2-Cu_2O	Thumba	6:1	1.6	60	5.5 kW, 2 bar	60	[76]

A wide variety of research has been carried out in this direction which aimed at investigating HC transesterification. The impact of the orifice vessel diameter on biodiesel purity can be examined [77]. Investigations of additional optimization and process progress through the combination of various cavitation (ultrasonic and hydrodynamic) for transesterification reactions using low energy would be very promising [78]. Therefore, the overall expense of transesterification reaction can be significantly diminished (Fig. 3). The severity of microbubbles destruction depends on the physical characteristics of the fluid; including, density, viscosity, vapor pressure, and the configuration of the geometrical variables of the orifice [79]. Regarding biodiesel generation, HC is notably proper from the aspect of energy and transesterification yield. Most of the investigations have been limited to laboratory-scale experiments, and the practical implementation of commercial objectives remains largely absent. This can be because of the economic limitation, lack of skills and also technological constraints that were a beginning for the growth and execution of the technique worldwide [80, 81].
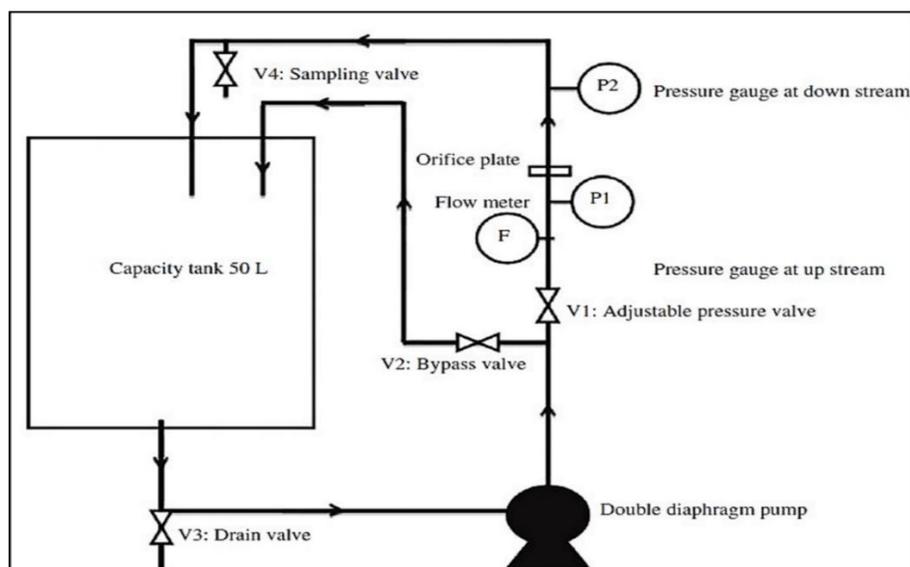
Fig. 3. HC reactor configuration for transesterification reaction [79]

Comparison of Ultrasonic Cavitation and Hydrodynamic Cavitation

According to Table 3, it can be observed that hydrodynamic cavitation is efficacious, owing to energy consumption and reaction time. The transesterification time was diminished in the order of hydrodynamic cavitation, ultrasonic cavitation, and mechanical stirring. It can be noticed that hydrodynamic cavitation $(8.7–75×10^{-4})$ g/J for methyl ester generation in the present paper is approximately 50–174, 39–87, 3–11, and 1–2 times more efficient than mechanical stirring $(0.05–1.5×10^{-4})$ g/J and ultrasonic cavitation $(0.1–1.9×10^{-4})$ g/J. Nevertheless, these comparisons are according to the various reactor capacity and raw material features. Therefore, the identical reactor capacity of various boosting procedures should be utilized regarding the mentioned comparison in terms of energy yield. Significantly, hydrodynamic cavitation appears to be preferable as compared to other boosting techniques in terms of bubble size, scale-up capability, transesterification time, energy consumption, and methyl ester purity.

Table 3. Comparison of hydrodynamic cavitation, ultrasonic cavitation, and mechanical stirring approaches

Procedure	Feedstock	Yield (%)	Yield Efficiency $(10^{-4}$ (g/J))	Reactor Capacity (L)	Ref.
UC	Waste Cooking Oil	89.2	12.2	15	[46]
HC		90	0.5	-	
HC	Rubber Seedoil	92.5	41.3	25	[64]
HC	Rubber Seedoil	97	9.1	50	[69]
HC	Rubber Seedoil	96.5	2.2	50	[70]
UC		93	0.5	-	
HC	Waste Frying Oil	93.5	27.5	10	[72]
HC	Waste Frying Oil	96.1	9.8	5	[73]
HC	Schleichera Oleosa Oil	95	5	10	[75]
UC		93.8	0.8	0.1	
HC	Thumba Oil	60	-	15	[76]
HC	Vegetableoil	98	33.5	10	[80]
UC		99	0.87	0.1	
MC		90	0.07	-	

It should be mentioned that the features of biodiesel generated through ultrasonic radiation are completely consistent with the ASTM standard and are within its limits. For example,

Maleki et al. [9] scrutinized the production of biodiesel from dairy waste oil applying the ultrasound-assisted technique. They revealed that the properties of the biodiesel are within the range of the ASTM standard. Furthermore, in another study, Maleki and Esmaeili [13] assessed the features of biodiesel generated from waste frying oil at the presence of ultrasonic radiation. The results demonstrated that the produced biodiesel is in good agreement with ASTM standard values.

Conclusion

Generally, biodiesel generation at a commercial scale is carried out using the conventional method of mechanical stirring along with heating through transesterification via oil source at the presence of alcohol and catalyst. However, the main drawback of the traditional approach to the transesterification process is its limited efficiency in terms of mass transfer, resulting in a slower process acceleration and significantly higher costs as compared to conventional diesel. Heretofore, various intensification approaches including HC, UC and microwave have been attempted to prevail over these limitations. Accordingly, it was discovered that UC is yet to be entirely achievable for biodiesel generation at a commercial scale. However, HC needs gentle reaction circumstances to conduct the transesterification process. This method offers several benefits, such as: reducing energy consumption, speeding up the reaction, improving the quality of alkyl ester, being eco-friendly and easy to perform, creating cavitation with a simple and low-cost technique, and scaling up without difficulty. More investigations are yet required to develop the current knowledge of HC in the design of the plate geometry, considering the biodiesel yield to conceive a sustainable and feasible pathway for fuel recuperation from renewable resources. It can be expressed that the output performance of the intensified approaches in biodiesel production are HU, UC and MS, respectively.

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