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Irradiation Enhanced Synthesis and Characterization of Biodiesel from Vegetable Oil-A Short Review

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Abstract: Depletion of petroleum resources continues to be an important global issue. To overcome this issue, biodiesel is gaining more and more importance as an alternative, renewable and sustainable fuel. Chemically biodiesel is ester of monoalkyl fatty acid derived through catalytic transesterification process from mostly non-edible vegetable oil. The transesterification process is influenced by the mode of reaction condition, molar ratio of alcohol to oil, type of alcohol, reaction time and temperature. Transesterification process by conventional heating needs more reaction time which is dramatically reduced by using suitable irradiation techniques like ultrasound, microwave or sunlight as heating sources. Other parameters like alcohol-oil ratio and quantity of catalysts are also influenced by the irradiation. Choice of catalyst along with the type of irradiation is also a critical parameter. Type and power of irradiation also influence some of the process parameters. In this paper, available literature on irradiation-enhanced synthesis of biodiesel with different combination of oil and catalysts has been reviewed.

Keywords: Biodiesel; Vegetable oil; Monoalkyl Fatty acid ester; Transesterification; Light; Ultrasound; Microwave

1. Introduction

With the advancement of industrialized civilization, conventional fuels are getting scarce and costly. Moreover emissions from their combustion pollute the environment. Alternative and non-polluting fuels are therefore, demand of the day. Hydrogen, natural gas or biofuels are among such alternative fuels that have high potential for mass consumption.

Biofuels are organic combustible matter that are derived from biomass; biofuels can be solid (wood or cow dung cake), liquid (alcohols) or gas (pyrolysis gas). The advantage of biofuel is that, they recycle carbon dioxide without increasing the net quantity of the same in the atmosphere, if their consumption is proportionate with their generation. For internal combustion engines, liquid biofuels can be of two types –bioalcohols and transformed oils. However, biofuel and biodiesel are not synonymous- according to a few scientists, biofuels can be of three generations. The first generation of biofuels includes edible oil used both for alcohol and biodiesel production, the second generation comprises biofuels and biodiesel derived from non-edible plant-products and the third generation includes biodiesels produced by the microalgae.

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According to the American Society for Testing and Materials Standard biodiesels are defined as *'monoalkyl esters of long chain fatty acids derived from renewable lipids such as vegetable oils or animal fats used in ignition engines'* [1].

Due to this similar structure as fossil fuel, biodiesel is accepted as a suitable substitute and no modification is required for the engine. The major advantages of biodiesel over the conventional diesel oil are its biodegradability, non-toxicity, low emission profile, easy availability of raw materials and similar chemical structure. Biodiesel is used either in the pure form or as a blend with fossil-diesel.

The history of exploring biodiesel is more than 100 years old. Rudolf Diesel tested the performance of an engine with peanut oil in 1900 in Paris [2]. But due to the low volatility, high viscosity, high flash point and residue after combustion they could not be considered as an engine-fuel. Hence modification of vegetable oils were necessary to make it suitable for injection in the engines were necessary. Trans-esterification is one such modification [3].

The technology usually employed to produce biodiesel, is transesterification of the vegetable oil. Many researches have shown that biodiesel production from non-edible vegetable oil is more economic than edible oil source [4]. Transesterification is the process of converting a vegetable oil into an ester using an alcohol (e.g. methanol, ethanol), in presence of a catalyst like sodium hydroxide or potassium hydroxide with glycerol as a byproduct [5]. In the conventional method, the necessary energy is provided by heating accompanied by mechanical mixing. It needs much more reaction time of more than an hour. Higher energy consumption, high equipment cost, usage of excess amount of alcohol and longer reaction time are the drawbacks of conventional method. Theoretically, each mole of biodiesel is generated out of 1 mole of alcohol and 1/3 mole of triglyceride. However, an excess of alcohol is usually added to increase the yield of biodiesel [6].

This reaction time can be minimized from one hour to five minutes by using different irradiations as sources of energy [7]. Irradiation energy interacts with the reactants at a molecular level, thus very efficient and rapid heating can be obtained. Since the energy is interacting with the molecules at a very fast rate, the molecules do not have time to relax and heat is generated at short times results speedy completion of reaction.

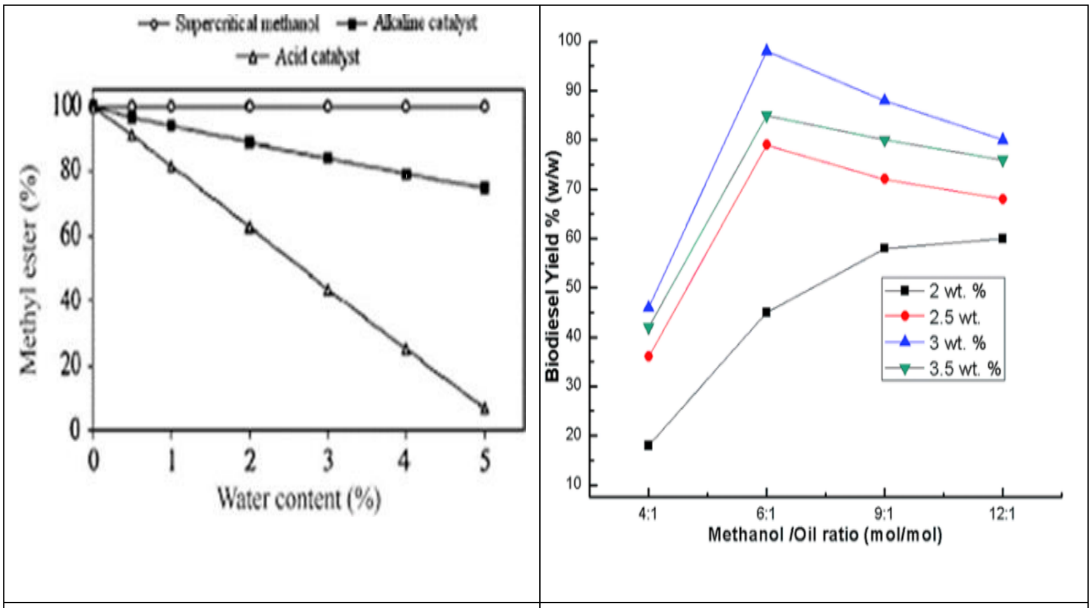
2. Oils generally used for biodiesel

It is difficult to get raw material (vegetable oil) for production of biodiesel. If the mono-unsaturated fatty acid content is high, kinematic viscosity, density and cold flow properties may improve but properties like cetane number or calorific value may deteriorate. On the other hand, with increasing chain length, the calorific value and cetane number increases, but some other properties like oxygen content, kinematic viscosity, density and cold properties are negatively affected [4].

A few oils used for production of biodiesel are rapeseed, soyabean, coconut, palm [8], sunflower [9], corn, ricebran [10], castor [11], karanja [12], tobacco seed [13] and Jatropa [14]. Sometimes waste cooking oils are also used for synthesis of biodiesel [15 -- 17].

3. Alcohols used for biodiesel products

The most used alcohol for biodiesel production is methanol; it does not form azeotropic mixture with water and hence easy to separate after use. Ethanol and isopropanol may also be used, but ethanol forms an azeotropic mixture with water. A critical factor is the water content. Water interferes with transesterification reactions when using alkaline catalyst and can result in poor yields of BD, high levels of soap, FFA and triglycerides [18].



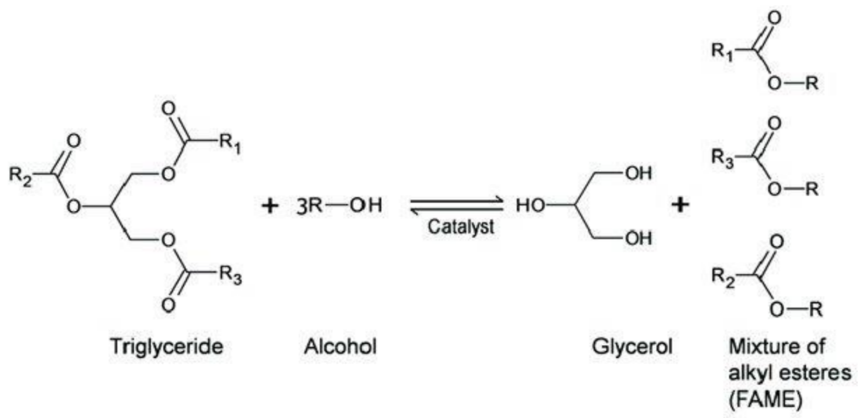
(a) **(b)**

Fig. 1: (a) Influence of water content on yield of biodiesel [19]; (b) Influence of methanol: oil ratio on yield of biodiesel [20]

Alcohol to oil molar ratio is an important parameter in biodiesel production. As this is a reversible reaction, one can increase the molar ratio of alcohol to obtain more biodiesel. Also if excess alcohol is added to the oil, more undesirable product glycerol is produced. Moreover it can dilute the catalyst concentration. Many researchers have shown that 6:1 alcohol to oil molar ratio leads to maximum production rate [21].

4. Transesterification mechanism

Synthesis of biodiesel through transesterification reaction refers to a catalytic chemical reaction involving vegetable oil and alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol(by product) [22 – 26].



R_1, R_2, R_3 = Hydrocarbon chain ranging from 15 to 21 carbon atoms

Fig. 2: Schematics of overall transesterification reaction [27]

Transesterification is the reaction of an oil or fat with an alcohol to form esters and glycerol. There are three reaction steps are involved in the transesterification process of triglycerides [28]. In the first step of reaction, triglyceride molecule reacts with an alcohol molecule (mainly used methanol) to produce diglyceride and a fatty acid alkyl ester. Then in the second reaction, diglyceride reacts with alcohol to form monoglyceride and another molecule of fatty acid ester. In the third reaction, monoglyceride reacts with alcohol to produce glycerol and a third molecule of fatty acid ester.

Transesterification is either catalytic (acid or base) or non-catalytic (using supercritical fluid) [29 – 33].

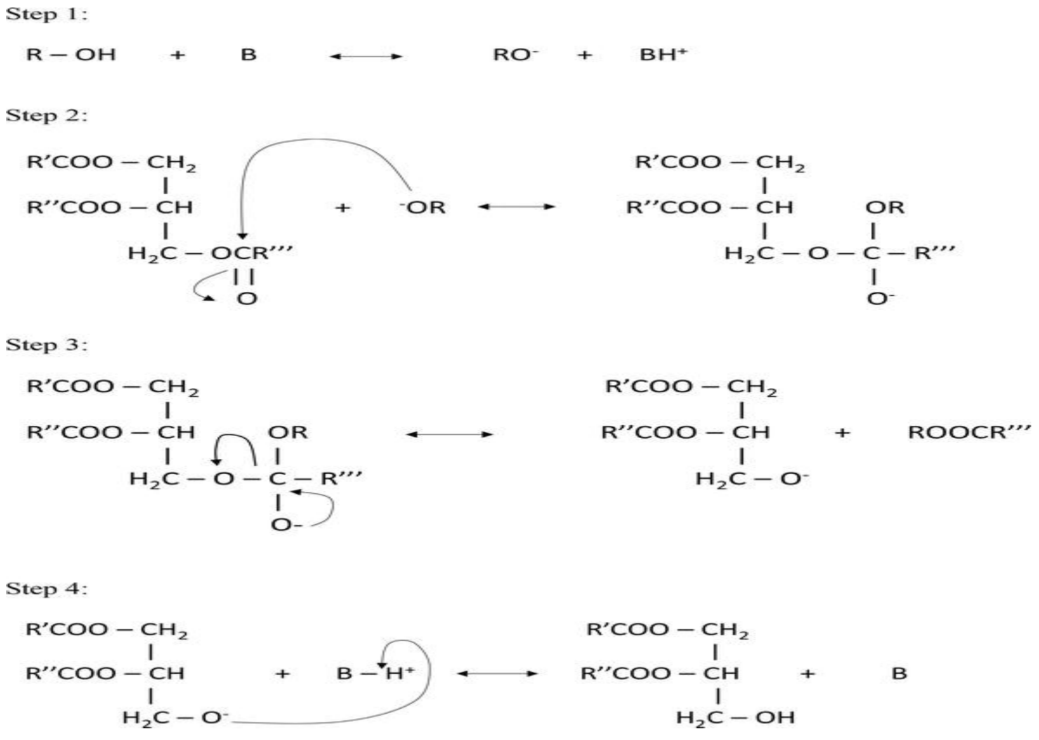


Fig. 3: Mechanism of base catalyzed transesterification [34]

For a base-catalyzed reaction, first a reaction of base with alcohol occurs to form alkoxide with the protonated catalyst. Then nucleophilic attack takes place at the carbonyl carbon of triglyceride molecule by alkoxide ion to form a tetrahedral intermediate. This intermediate is rearranged to give rise to alkyl ester and a diglyceride anion. Diglyceride anion deprotonates the catalyst to form active catalyst and diglyceride. Thus diglyceride and monoglyceride are transformed into alkyl ester (FAME) and glycerol using the same mechanism [35 – 38].

In case of an acid-catalyzed reaction, carbonyl oxygen is protonated by H^+ which results in cation formation. Then nucleophilic attack of alcohol occurs to produce tetrahedral intermediate. This intermediate is rearranged to release an alkyl ester (FAME) and proton catalyst [39 – 41].

For oils having high amount of free fatty acids, a two-step process, using two types of catalysts, is recommended [42]. First acid catalyst is employed for esterification of free fatty acid to ester. When free fatty acid level reaches less than 0.5-1%, then base catalyst is employed for transesterification step. But the major drawback of this process is the requirement of extra separation stages, washing and catalyst removal in both steps [43, 44].

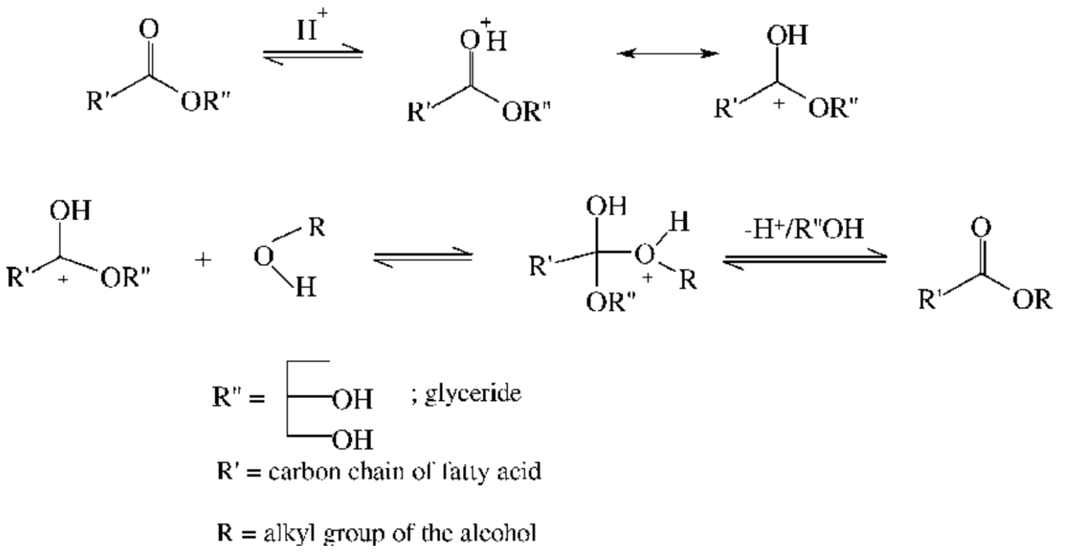


Fig. 4: Mechanism of acid catalyzed transesterification [45]

There may also be a few competitive side reactions. If water is present, especially at a high temperature, it may hydrolyze the triglyceride to diglyceride and free fatty acid. Another undesired side reaction is production of soap by the reaction of free fatty acid and alkaline catalyst [46].

5. Catalysts used for synthesis of biodiesel

The catalysts in the conventional transesterification reaction may be homogeneous or heterogeneous. The most common homogeneous catalysts are alkaline sodium hydroxide and potassium hydroxide. Acids may also be used as catalysts for oils with high fatty acids, but the rate of reaction is too low for industrial production and acids also need a neutralization after the reaction is over [47]. Alkaline catalysts are less corrosive than acids and gives faster reaction rate. Another drawback of acid catalyzed process is catalyst separation after the reaction is over. So alkaline catalyzed transesterification is more preferred than acid catalyzed processes [48].

Among the heterogeneous catalysts, alkaline earth oxides, alkali doped materials, transition metal oxides, hydrotalcites, mesoporous silicas, hetero-polyacids, acidic polymers and resins, waste carbon-derived solid acids or miscellaneous solid acids are included. Transition metal oxides like TiO_2 or ZnO act as photocatalysts under UV or sunlight in light-enhanced transesterification process [47].

6. General characteristics and standards of biodiesel

The American Society for Testing and Materials (ASTM) standard D6751and the Committee of Standardization in Europe (CEN) standard EN 14214 in Europe stipulate several quality specifications that must be met before biodiesel can be used as a direct fuel replacement or as blend with petroleum [49 – 52]. A summary of the standards of the ASTM and EN are given in Table-1 below:

Table 1: ASTM and EN standards for biodiesel [ASTM D6751 and EN 14214]

Property	**Unit**	**Limits**		**Test Method**	
		ASTM D6751	**EN 14214**	**ASTM D6751**	**EN 14214**
Viscosity at 40°C	mm^2/s	1.9-6.0	3.5-5.0	D445	EN ISO 3104
Flash point	°C	130	101	D93	ISO CD 3679e
Density at 15°C	kg/m^3	-	860-900	-	EN SIO 3675
Cetane number	-	47	51	D613	EN ISO 5165
Water content	mg/kg	-	500 max	-	EN ISO 12937
Methanol content	%(m/m)	-	0.2 max	-	pr EN 141101
Acid value	mg KOH/g	0.80 max	0.5 max	D664	pr EN 14101
Free glycerol	%(m/m)	0.020max	-	D6584	pr EN 14106

In India, IS-15607-2016 describes the standard for Fatty acid methyl ester (FAME). However the quality of blend biodiesel was governed by IS-15607-2005. In Table-2 a few parameters as stipulated in both the standards are compared.

Table 2: Comparison of Indian standards for blend biodiesel and FAME [IS-15607-2005 and 2016]

Property	**Unit**	**Limits**		**Test Method**	
		IS-15607-2005	**IS-15607-2016**	**IS-15607-2005**	**IS-15607-2016**
Viscosity at 40°C	mm^2/s	2.5- 6.0	3.5-5.0	ISO 3104	ISO 3104
Flash point	°C	120	101	-	ISO 2719
Density at 15°C	kg/m^3	860-900	860-900	ISO 3675	ISO 3675/ISO 12185/ D 4052
Cetane number	-	51	51	ISO 5156	ISO 5165
Water content	mg/kg	500	500	D 2709	ISO 3733/ ISO 6296/ ISO 12937
Methanol content	%(m/m)	0.2	0.2	EN 14110	EN 14110
Acid value	mg KOH/g	0.50	0.50	-	EN 14104/ASTM D 974
Free glycerol	%(m/m)	0.02	0.02	D 6584	D 6584/EN 14105/ EN 14106

7. Irradiation-enhanced synthesis of biodiesel using different irradiation sources

A group of irradiation-enhanced technology has been introduced for synthesis of biodiesel including photocatalysis, ultrasonication and microwave irradiation. The purpose of the irradiation is to provide more intimate contact and excitation of the reactant. A few advantages are there for the irradiation-enhanced synthesis of biodiesels over the conventional process - in most cases, the reaction conditions are moderate, the closer contact between reactants leads to a significant reduction of both catalyst and/or alcohol and higher biodiesel yield in less reaction time is reached [48].

Aim of this review is to compile the three above-mentioned techniques for the irradiation-enhanced synthesis of biodiesel and also to compare the processes as well as the quality of biodiesel obtained by such methods.

8. Ultrasound-enhanced synthesis of biodiesel

Sonochemistry refers to the application of the ultrasound with a frequency greater than the upper limit of human hearing (~20 kHz to 10 MHz) into chemical reaction.

Ultrasound energy is a useful tool to enhance both the mass transfer and chemical reactions resulting in shorter reaction time, cheaper reagents and less extreme physical conditions. Ultrasound wave alternately compresses and stretches the molecular spacing of the medium during the chemical process and easily can make fine emulsions from immiscible liquids. By introducing high power ultrasound into a liquid medium, the sound waves are transmitted in the fluid and create alternating high pressure (compression) and low pressure (rarefaction) cycles, with rates depending on the frequency. During the low pressure cycle, high intensity ultrasonic waves create small vacuum bubbles or voids in the liquid. Acoustic cavitation is the growth and collapse of cavitation bubbles, which when exploded, generates an increase in temperature in the reaction medium. This phenomenon is able to increase the speed of the reaction and reduce the reaction time [53]. Among the irradiation enhanced processes for synthesizing biodiesel ultrasonic process is the most suitable for large scale production [48].

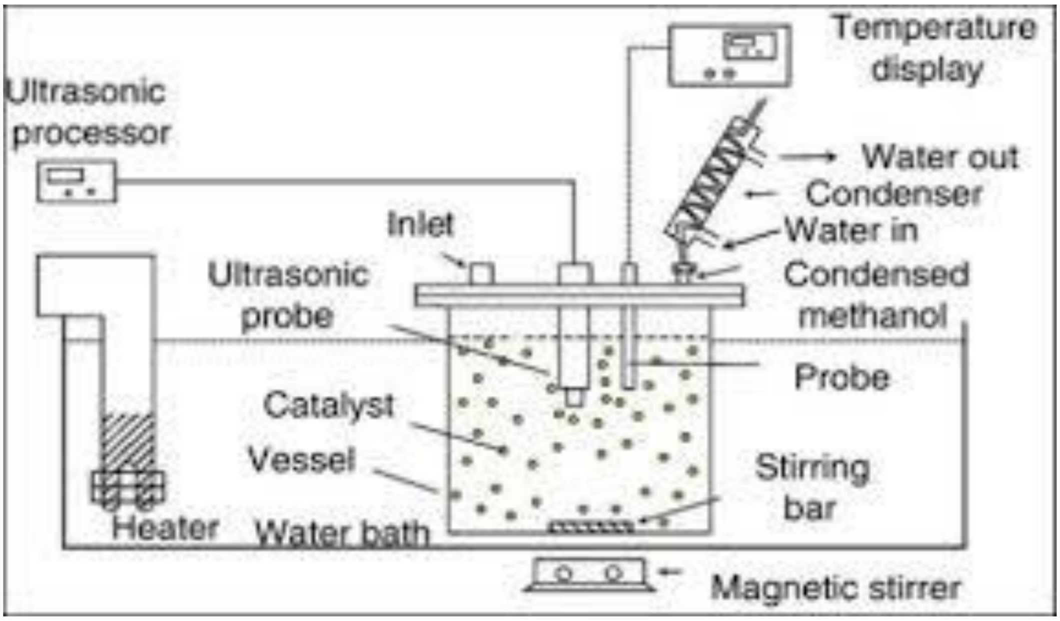


Fig. 5: Ultrasound enhanced synthesis of biodiesel - a schematic diagram for the Set-up [54]

There may be three types of devices for introducing ultrasound in the reaction mixture – ultrasonic bath, ultrasonic probe or horn and sonochemical reactor. Bath type sonicator passes ultrasound indirectly through the water taken in the bath to the solution whereas probe type sonicator inserts ultrasound directly to the reaction mixture [55]. Hence in bath type sonicator, the distribution of sound energy may not be uniform and this is a limitation of the bath type sonicators.

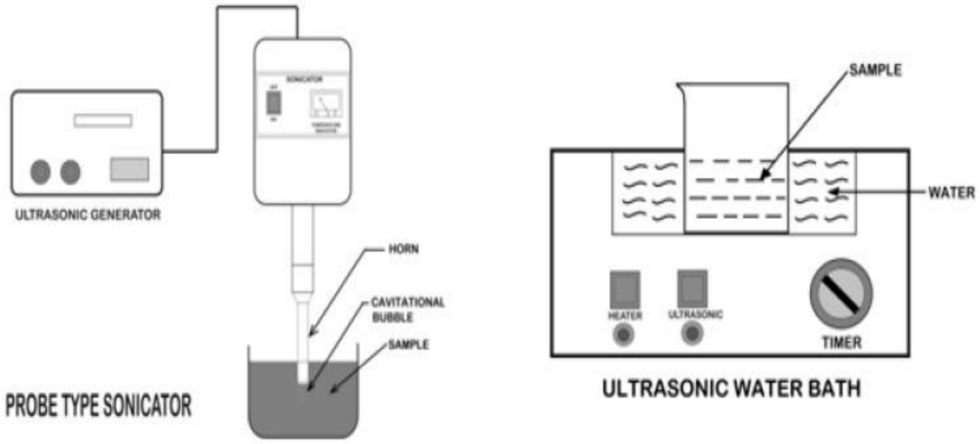


Fig. 6: Arrangements of probe and bath type sonicators [55]

In the study by Georgogianni et al. [56] an ultrasonic probe (24 kHz, 200W) was used in the transesterification reaction of sunflower oil with methanol. After 20 min of reaction, a conversion of 95% was obtained at alcohol to oil molar ratio of 7:1 in the presence of 2% of the sodium hydroxide catalyst. The same authors obtained 96% yield in 40-60 minutes with rapeseed oil using a bath type ultrasonicator of same power [57]. Fan et al. [58] also performed biodiesel production by using ultrasonic probe (40kHz, 200W). They used cotton seed oil and methanol at alcohol to oil molar ratio of 6:1 and 1% potassium hydroxide. In 5 min of reaction, it reached 96% biodiesel yield. A 99% biodiesel yield was obtained by Santos et al. [59] by using ultrasonic probe (40kHz,200W) at methanol to waste cooking oil molar ratio of 9:1 and 3% sulfuric acid catalyst. Babajide et al. [60] obtained 96.8% yield with waste cooking (sunflower and soyabean) oil, 6:1 methanol and 0.75% KOH in 20 minutes using 24kHz probe type sonicator. Hyyan et al. [61] obtained 96.3% yield with methanol (7.5:1) using 0.7% H_2SO_4 catalyst in 300 minutes using 40 kHz bath type sonicator. Kumar et al. [62] developed biodiesel from coconut oil catalyzed by potassium hydroxide. An ultrasonic probe was used at 24kHz, 200W. After 7 min of reaction , a maximum conversion of 98% was obtained with an ethanol to oil molar ratio of 6:1, 0.75% catalyst concentration. Rapeseed oil at 45°C was used by Xuan et al. [63] with 0.5% methanol and 4W sonication through a probe to get a yield of 80% in 20 minutes. Deshmane et al. [64] produced biodiesel using an ultrasonic bath with frequency of 25kHz. In this study, the highest conversion 80% was obtained at isopropanol to palm oil molar ratio of 5:1 and 5% catalyst concentration. Thanh et al. [65] also produced 99% biodiesel yield from canola oil by using ultrasonication (20 kHz) at methanol to oil molar ratio of 5:1 and 0.7% sodium hydroxide catalyst. 98% biodiesel yield was achieved by Santos et al. [66] from *oreochromisniloticus* oil catalyzed by sulfuric acid. The reaction was carried out under ultrasonication (40kHz) at methanol to oil molar ratio of 9:1.

A few process parameters are influenced by the ultrasound. Reaction time is reduced from the order of hours in conventional process to the order of minutes by using ultrasound. Due to an efficient dispersion, efficiency of catalysts, especially that of heterogeneous catalysts are increased; required quantity of the catalyst is also reduced. In conventional transesterification, energy is required both for agitation and for heating the reaction mixture. Since ultrasound mixes and heats up the reaction mixture at a time, some energy is saved. Alcohol: Oil ratio is an important parameter – by using ultrasound, it is observed that less quantity of alcohol is required compared to the conventional process for same yield of biodiesel [1].

9. Microwave-enhanced synthesis of biodiesel

Among the sources of irradiation, microwave is an important one [67, 68]. Biodiesel can also be produced using microwaves. Microwaves are part of electromagnetic waves between the radio frequency and inferred frequency ranges (2.45GHz) [69, 70]. Conventional heating process in biodiesel production requires large amount of heats and the temperature is applied to the material surface only whereas microwave systems can directly transfer thermal energy into interior molecules of the reactants [71]. Controlled and accurate heating, short reaction time, quality and property improvement are the keys to choose microwave technique over the conventional heating process [72].

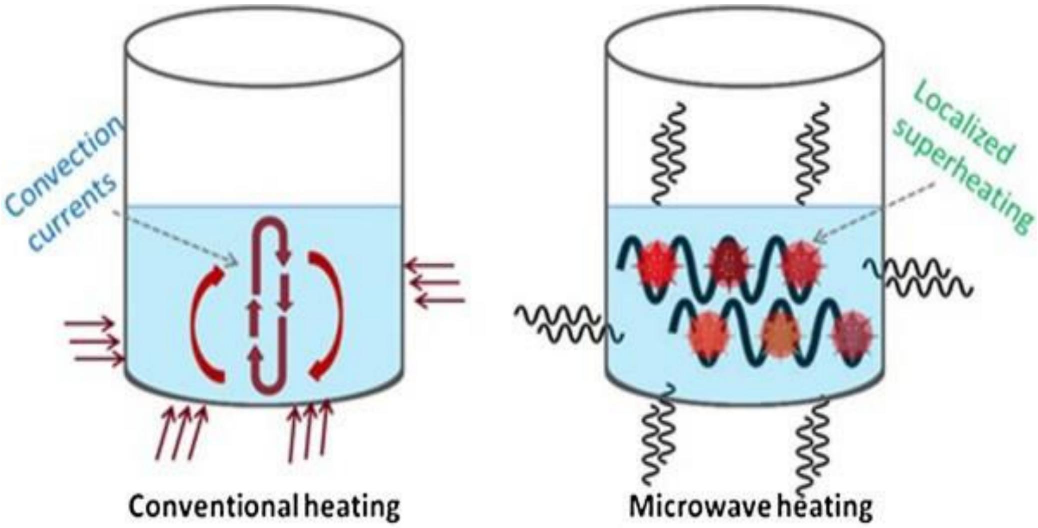


Fig. 7: Microwave enhanced synthesis of biodiesel - a schematic set-up [73]

Microwave irradiation rises the temperature of the whole volume evenly and simultaneously whereas in conventional heating the reaction mixture in contact with the vessel wall is heated first. If a molecule possesses a dipole moment, when it is exposed to microwave irradiation, the dipole tries to align with the applied electric field. Since the electric field is oscillating, the dipoles constantly try to realign to follow this movement. This continual reorientation of the molecules results in friction and thus heat . It needs less reaction time [74].

One major issue of using microwaves is the high cost of the reactors – researchers modified domestic microwave ovens into laboratory scale reactors to overcome such problem [75].

Patil et al. [38] produced 92% biodiesel yield from waste cooking oil by using microwave irradiation at methanol to oil molar ratio of 9:1 and 2% potassium hydroxide catalyst. 98.85% biodiesel yield was reported by Azcan et al. [76] at 6:1 methanol to waste frying oil molar ratio catalyzed by 1.5% sodium methoxide under microwave irradiation. Hincapé et al. [77] also performed biodiesel production by using microwave irradiation. They used castor oil and ethanol at alcohol to oil molar ratio of 10:1 and 1.5% potassium hydroxide. Li et al. [78] observed 93.51% biodiesel from soybean oil catalyzed by sodium potassium tartrate doped zirconia under microwave irradiation.

Process parameters that can influence the microwave-enhanced production of biodiesel are catalyst type and quantity, reaction time, microwave power, fatty acid and water content, reaction temperature and alcohol to oil ratio.

It was observed that an increase in microwave power generally increase the percent yield upto a critical value, after that the yield decreases due to damage the molecular structure of triglyceride at high power microwave irradiation Groisman and Gedanken [79]. Sherbiny et al. [74] obtained 83% yield of biodiesel from Jatropha oil in 30 minutes using 1% KOH and 1200 W power of microwave. However Lin and Chen [80] achieved 90% yield with the same raw material and catalyst using 950W microwave in 10 seconds.

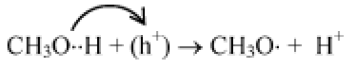
The same trend is also found in case of irradiation time; increase in irradiation time increases the yield upto a critical value. Castor oil with 5% H_2SO_4 catalyst and 200W microwave power yielded 43% biodiesel in 10 minutes, 54% in 20 minutes and 93% in 180 minutes [81].

Regarding heterogeneous catalysts, performance of CaO is good with microwave. Particlesize of the solid catalyst is also a critical factor. Khemthong et al. [82] used CaO powder with palm oil (olein) under 900W microwave. They obtained 96.7% yield in only 4 minutes. Soyabean oil yielded 96.6% biodiesel in 60 minutes using 3% CaO nanoparticles under 300W microwave [83]. In 15 minutes the yield was 56.2%.

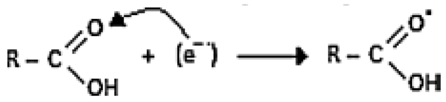
Dielectric constant of a solution is a critical parameter to be considered for biodiesel production using microwave irradiation. It was observed that using microwave, quantity of alcohol required can be reduced compared to the conventional process. It was also observed that a mixture of methanol and ethanol performed better under microwave irradiation [84]. Optimum reaction temperature should be in the range 50-60°C depending upon the boiling point of the alcohol used.

10. Enhanced photocatalytic synthesis of biodiesel

Solar energy is the ultimate source of energy on earth. Solar energy is the most abundantly available renewable energy while the world is facing a crisis of the conventional energy. The term photocatalysis mean accelerating a chemical reaction assisted by light. When light having energy greater than the band gap of the semiconductor photocatalyst falls on it, an electron hole pair is generated which promotes the chemical reaction [85]. Photocatalysts enhance the reaction of conversion of free fatty acids to fatty acid alkyl esters [86]. In base-catalyzed transesterification reaction a proton is removed from the alcohol, the alcohol becomes more nucleophilic. Hence in a base-catalyzed reaction using NaOH as base, alcohol undergoes oxidation. If a heterogeneous semiconductor photocatalyst such as ZnO is used instead of base catalyst, the alcohol attracts the hole which is generated in by the semiconductor catalyst as sunlight or UV light falls on it. Due to high oxidative potential, the photo-generated holes (h^+) may react with CH_3OH adsorbed on the catalyst surface, producing hydrogen ions (H^+) and $CH_3O\bullet$ radicals. Thus the alcohol, a hole-scavenger, attracts the hole and gets oxidized. Photocatalytic oxidations of primary, secondary, tertiary alcohol have been studied with TiO_2 particles suspended in aqueous solution. Thus the photocatalytically generated holes oxidize alcohol into carbonyl compound. Similar mechanism works in transesterification reaction. Alcohol (methanol) is oxidized by the TiO_2 particles suspended in it under sunlight or UV light. Thus the $CH_3O\bullet$ radical reacts with the triglycerides, the free fatty acids present in vegetable oil to produce fatty acids of methyl esters. Photogenerated holes and electrons are consumed in the following way as proposed by Corro et al. [87].



$$CH_3O\cdot\cdot H + (h^+) \rightarrow CH_3O\cdot + H^+ \qquad (1)$$



(2)

Solar photocatalytic reactions have been popular and effective over time because the source of energy is completely inexpensive and environment friendly. But many of the photocatalytic reactions take place under UV lamp because light of ultraviolet spectrum may excite the photocatalyst with excitation energy higher than its band gap. Low to medium pressure mercury lamps within the UV range for photocatalysis degradation is used as well [88]. In different methods of waste glycerol conversion the test runs are performed in the batch and semi-batch reactors equipped with Xe lamps as a light source [89]. Much higher hydrogen productivity is observed for the Titania modified by noble metals than for transition metal used for modification. Thus UV light from Xenon lamps is another alternative for solar light. However sunlight still remains the most feasible source for conducting photo catalytic reactions. Corro et al. [87] reported the synthesis of biodiesel from *Jatropha curcus* seed oil using heterogeneous semiconductor photocatalyst such as ZnO, SiO_2 and a mixture of ZnO/SiO_2. The photocatalysts were characterized by BET surface area, UV-vis spectrometry, FTIR and XRD analysis. Specific surface area of the ZnO/SiO_2 was 160 m^2/g. The source of UV light was a 3W mercury lamp. They achieved about 100% conversion using a particular ratio of catalyst to oil keeping the methanol to oil ratio at 12:1. The activity of the catalyst remained unchanged even after 10 cycles.

Oloruntoba and Hamza [90] synthesized 45.2 % ZnO /49.6% SiO_2 (by weight) by mechanochemical route and utilized it for photocatalytic transesterification of waste cooking oil under visible light irradiation provided by a 500W halogen lamp; methanol: oil ratio was 12:1. A blank photochemical experiment was also conducted without the photocatalyst. Within 1 hour, yield was 87% for the photocatalytic process whereas for the photochemical process it was only 35%. The catalysts were characterized by XRD, UV-vis spectrometry, SEM and XRF.

TiO_2 has wide applications as a photocatayst, but other than that when it is treated with H_2SO_4 it forms SO_4^{-2}/TiO_2 which also reportedly increases the yield of biodiesel through transesterification. Carlucci et al. [91], Chen et al. [92] and Peng et al. [93] reported this where TiO_2 can be used as a heterogeneous catalyst but not as a photocatalyst.

11. Combination of irradiation enhanced processes

There are a few reports on the simultaneous application of ultrasound and microwave irradiations for biodiesel production [94 – 96]. Martinez-Guerra and Gude [97] used sodium hydroxide catalyst at 0.75 wt%, methanol-to-oil ratio of 6:1 and the combined irradiation for 2 minutes to achieve a yield of 98%. Ardebili et al. [98] showed that the overall production cost decreased by using combined microwave and ultrasound. They have taken a catalyst concentration of 1.09% and a methanol-to-oil molar ratio of 7:3.1 at 58.4°C to get a yield of 97% in about 2 minutes.

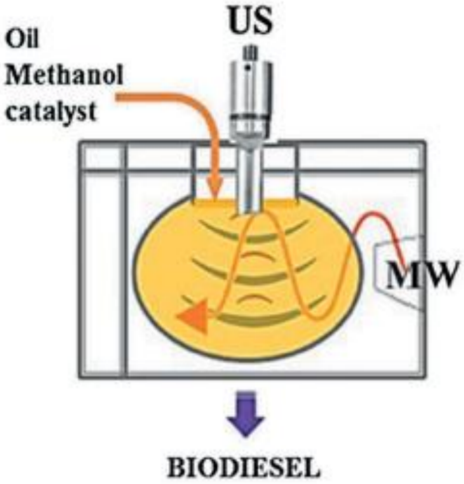


Fig. 8: Simultaneous use of microwave and ultrasonic for biodiesel production [97]

12. Comparison of the three irradiation-enhanced processes in biodiesel production

In terms of biodiesel production with different irradiation, main comparable factors are heating mechanism, reaction time, energy consumption etc. Transesterification reaction performed under conventional heating accompanied with mechanical mixing takes longer processing time (1-2 h) as heat energy is transferred to the raw materials through convection, conduction and radiation. High energy is consumed in conventional heating process. The reaction time is significantly reduced by applying ultrasound, microwave, photo-catalytic irradiation in transesterification of biodiesel.

Microwaves (2.45 GHz) produce dielectric heating at molecular level of raw materials which results the uniform heating and mixing in the reaction mixture at short time period. On the other hand, ultrasound induces continuous rarefaction and compression cycles of acoustic waves which produces micro bubbles to increase the activation energy as well as mass transfer rate of the reaction mixture, thus reduces the reaction time [99]. Ultraviolet lights can facilitate Transesterification reaction for synthesis of biodiesel. In such cases, a suitable photo-catalyst is required. TiO_2, ZnO are among the efficient photo-catalysts used for production of biodiesel.

Refaat et al. [100] described the comparison of three processes in biodiesel production in his report. They produced 95.79% biodiesel in 60 minutes by conventional heating process at 6:1 methanol to waste vegetable oil molar ratio and 1% potassium hydroxide catalyst. This reaction was also carried out under ultrasound irradiation by keeping all reaction conditions same. 98.26% biodiesel was achieved in 5 min under this technique. Again, microwave irradiation was employed in the third set up with same reaction condition. 100% biodiesel yield was observed in 2 min. This was the clear evidence of irradiation mechanism as time saving, energy efficient and sustainable route of biodiesel production.

13. Conclusion and future perspectives

The present review summarized various irradiation-enhanced transesterification processes for production of biodiesel from vegetable oil and alcohol. Irradiations like light, ultrasound or microwave in presence of suitable catalysts can enhance the rate of reaction thereby reducing reaction time. Amount of catalysts and alcohols required are also reduced by irradiation improving the overall economy of the process. Combination of two irradiations may further enhance the rate and economy. However most of the available reports are of laboratory scale and scaling-up of irradiation-enhanced processes are challenges to the engineers rather than the scientists. Development of suitable catalysts suitable for each of the irradiation-assisted processes are also a major issue. Combination of conventional with irradiation- enhanced process or application of more than one irradiation may be examined for process intensification.

To combat air pollution due to the emissions generated out of the fossil fuels, especially petrol and diesel, mass production of biodiesel should be explored in an economic and environment-friendly way.

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