Fuel Processing Technology 116 (2013) 241–249

Contents lists available at SciVerse ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Ultrasound assisted interesterification of waste cooking oil and methyl acetate for biodiesel and triacetin production

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ARTICLE INFO

Article history:
Received 21 February 2013
Received in revised form 14 July 2013
Accepted 14 July 2013
Available online xxxx

Keywords:
Biodiesel
Waste cooking oil
Interesterification
Process intensification
Ultrasound

ABSTRACT

Intensification of the interesterification reaction of waste cooking oil with methyl acetate using potassium methoxide as a catalyst has been carried out using ultrasonic horn (frequency of irradiation of 22 kHz and rated power of 750 W). Experiments have been performed at different operating parameters viz. reaction temperature (30, 40 and 50 °C), oil to methyl acetate molar ratio (over the range of 1:4 to 1:14), catalyst concentration (0.5, 1.0 and 1.5% by weight of oil) and amplitude of ultrasound (40, 50, 60 and 70%) with an objective of understanding the effect of important operating parameters on the extent of conversion of waste cooking oil to the ester. It has been observed that maximum yield (90%) of biodiesel from waste cooking oil using sonochemical reactors was observed at a molar ratio of 1:12, catalyst concentration of 1.0% and temperature of 40 °C. It is also observed that higher conversion was obtained in the presence of ultrasound as compared to the conventional method. Kinetic studies have been carried out to determine the rate constant by fitting the obtained experimental data to a second-order rate equation. It has been observed that rate constant increases with an increase in temperature and the activation energy is found to be 56.97 kJ/mol.

1. Introduction

Biodiesel is generally referred to as fatty acid esters, which can be essentially synthesized from oils or fats using the esterification based reactions. Biodiesel has several advantages over petroleum derived diesel such as biodegradability, non-toxicity, lower harmful emissions, higher flash point, excellent lubricity and superior cetane number [1]. Moreover, biodiesel is essentially free of sulfur and the engines fuelled by biodiesel emit significantly fewer particulate matters, residual hydrocarbons (due to near complete combustion) and less carbon monoxide as compared to the engines operating on conventional petrobased diesel [2]. Due to the depletion of petroleum reserves and increased environmental concerns, synthesis of alternative fuels has been a significant point of interest to the researchers. Overall, biodiesel has a huge potential to replace exhaustible fossil fuel, ensuring the sustainability of human development and energy sources [3]. It is, however, estimated that the cost of biodiesel is approximately 1.5 to 2 times higher than that of the petroleum based diesel fuel [4]. The reasons for the higher price of biodiesel are as follows: a) 70–95% cost of biodiesel synthesis process is from the cost of raw materials such as food grade vegetable oils [5] b) low rates of reaction due to mass transfer limitations in the heterogeneous reaction system and c) difficulty in the separation of biodiesel from the side product and unreacted alcohols giving lower yields.

The production cost of biodiesel can be reduced by using waste cooking oil (WCO) as a starting raw material, which is less expensive than pure vegetable oil and also by employing interesterification process instead of the more commonly used transesterification process for biodiesel production. The interesterification of oils and fats with methyl acetate provides a promising alternative to transesterification because of the formation of triacetin instead of glycerol. This complex reaction is composed of three consecutive reversible reactions, which are shown in Scheme 1 [6]. Triacetin is used mainly as a plasticizer and a gelatinizing agent in polymers and explosives and as an additive in tobacco, pharmaceutical industries, and cosmetics. Recent studies have also shown that triacetin may be added to the formulation of biodiesel (up to 10% by weight) and the blended biodiesel still meets the quality standards set by ASTM D6451 and EN 14214 because of its mutual solubility [7]. Interesterification has been mostly studied in the presence of enzymes [8–10] or under supercritical conditions [3,11–14]. Supercritical and enzymatic methods of interesterification have their own disadvantages. The main disadvantages of supercritical method include (a) operations at very high pressures (20–40 MPa); (b) requirements of high temperatures (350–400 °C) resulting in much higher heating and cooling costs; (c) high oil: methyl acetate ratios (usually set at 1:42) [12] and finally the supercritical method entails higher costs for the evaporation of the unreacted methyl acetate. The drawbacks of enzymatic route of interesterification are significantly higher production costs [15] as well as difficulty in manufacturing at larger scales due to the need for a careful control of the reaction parameters and inherent slowness of the reaction [16].

Based on this analysis, it can be established that there is a need to develop sustainable process intensification technology for biodiesel production from WCO sources based on interesterification with an

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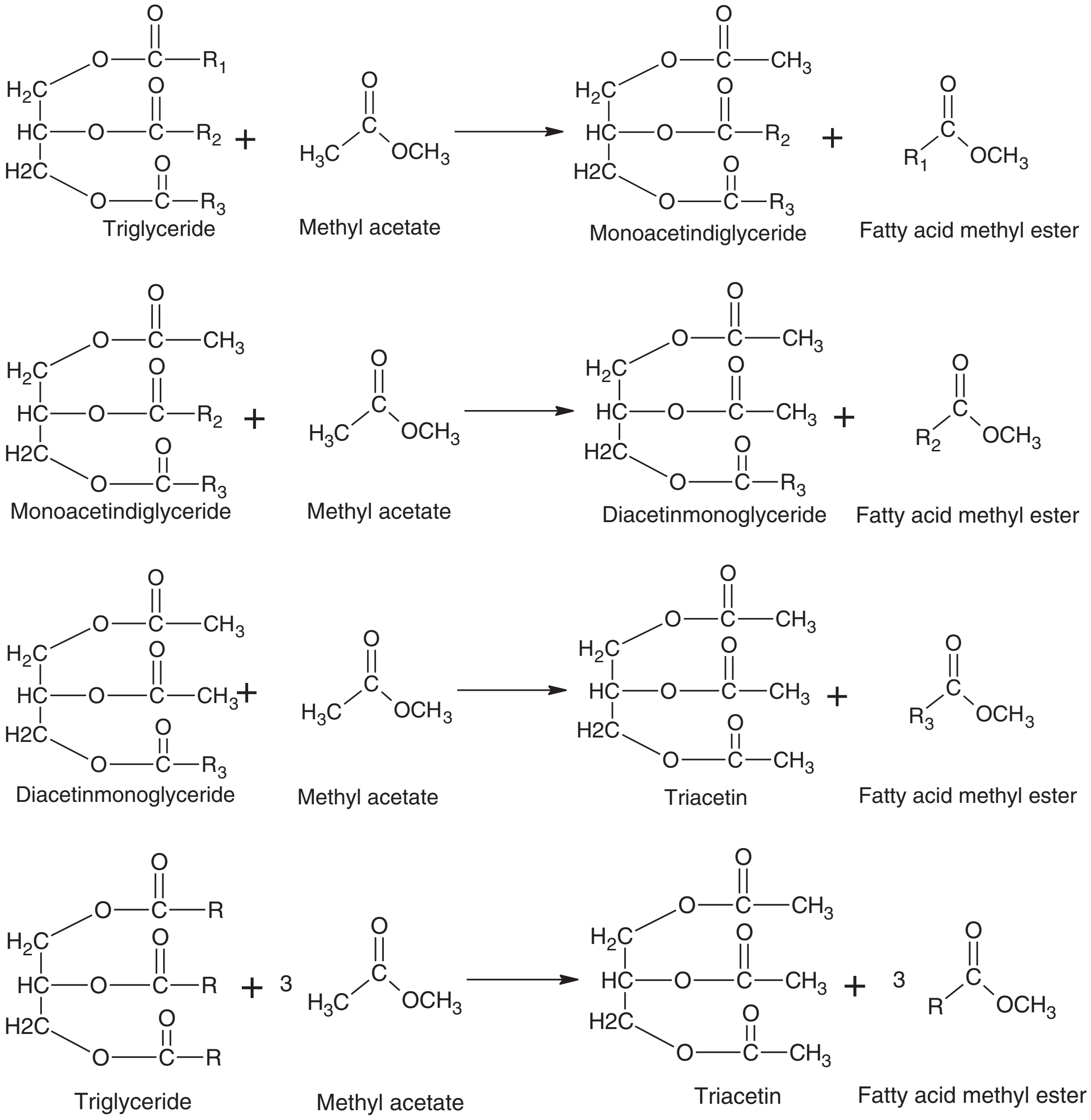
http://dx.doi.org/10.1016/j.fuproc.2013.07.004



Scheme 1. Interesterification reaction (Initial 3 equations show the individual steps whereas final equation gives the overall reaction).

objective of reducing the cost of processing. Cavitational reactors can offer a useful energy-efficient process intensification approach for biodiesel production as compared to other approaches for intensification such as microwave irradiation, oscillatory flow reactor, microchannel reactor, addition of co-solvent and supercritical uncatalyzed transesterification [17]. However, a careful study of the existing literature indicates that there has been absolutely no study related to the use of cavitational reactors for intensification of synthesis of biodiesel and triacetin using the interesterification reaction route. With this background, the present work deals with the intensification of interesterification reaction using sonochemical reactors, which are based on the generation of cavitation events due to the pressure fluctuations induced by the incident ultrasound waves. The interesterification reaction of pretreated WCO has been carried out in the presence of potassium methoxide as a catalyst using ultrasonic horn. Potassium methoxide has been selected as the catalyst for interesterification reaction due to the fact that it gives higher yield of biodiesel in interesterification reaction as compared to other catalysts such as potassium hydroxide, or PEGK (Polyethylene glycol complex with potassium). Experiments have been performed in the presence of potassium methoxide as a catalyst at different temperature, methyl acetate to oil molar ratio, catalyst concentration and amplitude to investigate the dependency of biodiesel yield from WCO. Kinetic constant as well as activation energy for the interesterification reaction have been also determined at optimum operating conditions. Also, the properties of the synthesized biodiesel from these methods have been evaluated in order to match with ASTM standards.

2. Material and methods

2.1. Materials

Waste cooking oil was procured from a local restaurant (Garnish Restaurant, King's Circle, Mumbai, India). Analysis of the WCO (Table 1) indicates that it is mainly composed of 91% unsaturated fatty acids (linoleic and oleic acids) and 9% saturated fatty acids (palmitic and stearic acid). Table 1 also shows the properties of waste cooking oil used as the starting raw material. Methyl acetate, potassium hydroxide pellets (LR grade), ortho-phosphoric acid, molecular sieves (3°A) used in the experimental work were procured from S.D. Fine Chem. Ltd., Mumbai. The weak anion-exchange resin (Indion 860) was obtained from Ion Exchange Ltd., Mumbai. Acetonitrile and acetone

Table 1
Composition and properties of waste cooking oil.

Property	Value
Linoleic acid (%)	73.4
Oleic acid (%)	18.3
Palmitic acid (%)	6.7
Stearic acid (%)	1.6
Saponification value (mg KOH/g of oil)	198
Density (kg/m^3)	930
Acid value (mg KOH/g oil)	4.3
Viscosity (mm^2/s)	54.3

(HPLC grade) used as solvent for HPLC analysis were procured from Hi Media, Mumbai. Methanolic potassium methoxide (33% by weight) was procured from Spectrochem Pvt. Ltd., Mumbai whereas methyl oleate and methyl linoleate standards were procured from Sigma-Aldrich. All the chemicals were used as received from the supplier without any purification, except for the waste cooking oil used in the experiments.

2.2. Experimental methodology

2.2.1. Pretreatment of waste cooking oil

A series of pretreatment processes were undertaken prior to the interesterification reaction of the WCO for biodiesel production. Pretreatment of WCO consists of physical treatment for removing the suspended solid contaminants by filtration and repeated water washing for the separation of water soluble salt impurities present in the WCO. After the water washing, dehydration was carried out by heating the sample at 80 °C under a vacuum of 25 mmHg for 10 min to remove the traces of water. Deacidification of WCO has been then carried out by adsorption using ion exchange resins to reduce the acid value of the WCO from 4.3 to 0.4. Experiments have been carried out by adding 1 wt.% of weak anion exchange resin (Indion 860) to the WCO in the presence of stirring at 800 rpm maintained for 3 h at 273 K. Weak anion exchange resin (Indion 860) was used for deacidification of WCO because it has excellent adsorption capacity of 491 and 532 mg/g of resin for unsaturated and saturated fatty acids respectively as established in our previous work [18]. After the adsorption treatment, cooking oil was separated from the anion exchange resin and this pretreated waste cooking oil has been used as the raw material in the interesterification reaction for the biodiesel production.

2.2.2. Interesterification of pretreated waste cooking oil

The interesterification experiments were performed in a 100-mL three-neck batch reactor. The three openings in the reactor are used for accommodating the condenser (to condense the methyl acetate evaporated during reaction), for the introduction of ultrasonic horn or stirrer (based on the approach of ultrasound assisted or the conventional approach) and for inserting the temperature sensor to monitor the temperature during the reaction. The schematic of the experimental setup has been shown in Fig. 1. The reactor was initially charged with vegetable oil and methyl acetate and heated to the desired reaction temperature. Once the desired temperature was reached, catalyst was added to the reactor, at which point the reaction can be considered to start. Several samples were collected at different pre-designated times and were immediately quenched using equimolar amount of ortho-phosphoric acid to arrest the progress of the reaction in the withdrawn samples. After this treatment with ortho-phosphoric acid, the samples were washed with water in order to remove the excess catalyst from the mixture. Finally, a molecular sieve (3°A) was added to each sample to adsorb the trace amount of moisture. Samples were then refrigerated until the final analysis was carried out using HPLC.

The different operating parameters used in the present work, to optimize the yield of biodiesel from waste cooking oil, include oil to methyl acetate molar ratio (OMAMR) (1:4, 1:6, 1:8, 1:10, 1:12 and 1:14), catalyst concentration (0.5, 0.75, 1 and 1.25% by weight of the charged oil), temperature (30, 40 and 50 °C) and percentage amplitude of ultrasonic horn (40, 50, 60 and 70%). Experiments were also performed using conventional stirring approach under optimized set of operating parameters to establish the degree of intensification obtained due to the use of ultrasonic irradiations. The setup for stirring is very similar to that shown in Fig. 1, except for the fact that in the conventional method an overhead stirrer has been used instead of an ultrasonic horn. A six-blade turbine with a diameter of 1.5 cm was used as the stirrer and the operating speed used in the work was 1000 rpm. All experiments were carried out in duplicate and the reported values are the average of the individual runs. The experimental errors were within 2% of the reported average value of biodiesel yield.

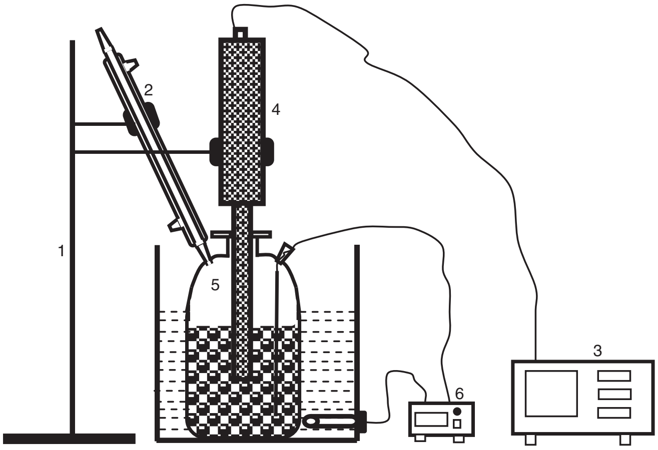


Fig. 1. Experimental setup for interesterification reaction. 1. Stand support. 2. Condenser. 3. Ultrasonic generator. 4. Ultrasonic horn. 5. Reactor. 6. Temperature controller.

2.3. Analytical methods

The acid value of the waste cooking oil in the first stage (pretreatment) was determined by the acid-base titration technique. For this analysis, 5 g of sample is transferred into a conical flask containing 20 ml of neutralized ethanol. The mixture was titrated with 0.003 N KOH using phenolphthalein as an indicator to determine the free fatty acid present in the solution. The observed end point is colorless to pink.

The fatty acid compositions in the WCO were determined by converting all the fatty acids into the corresponding fatty acid methyl esters followed by gas chromatography (GC) analysis using BP-X70 column. Fatty acid methyl ester content in the reaction mixture was analyzed on HPLC using Agilent Eclipse XDB C-18 column, with dimensions of 4.6 × 250 mm using RI detector. The samples were analyzed isocratically using mobile phase of acetonitrile: acetone (70:30) with 1.5 ml/min flow rate. Samples were prepared by using 10 µl of the reaction mixture diluted with 10 ml of mobile phase. A typical HPLC chromatogram for interesterification product identification has been shown in Fig. 2. The concentration was calculated based on the area under the peak for the retention time of standard samples of methyl oleate and methyl linoleate procured from Sigma-Aldrich. Based on the reaction stoichiometry, the percentage biodiesel yield was calculated from the product formation using the extent of completion of reaction under equilibrium conditions. Density [ASTM D7777], flash point, kinematic viscosity [ASTM D445], and acid value [ASTM D664] of final interesterified product have also been evaluated.

2.4. Kinetic constant and activation energy

The interesterification reaction progresses in three consecutive reversible reaction steps [19]. As shown in Scheme 1, interesterification begins with the reaction of triglyceride and methyl acetate to produce

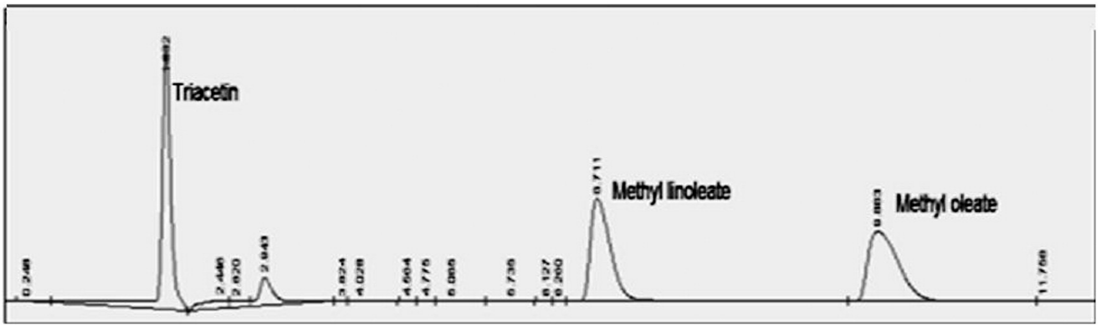


Fig. 2. HPLC chromatogram for identification of interesterification products.

monoacetindiglycerides and one mole of methyl ester. The monoacetindiglycerides further react with methyl acetate to yield diacetinmonoglycerides and another mole of methyl ester. The diacetinmonoglycerides finally react with methyl acetate to produce one mole of methyl ester and triacetin each. As interesterification reaction is reversible in nature, all the experiments were carried out at higher methyl acetate to oil molar ratio than that required as per the reaction stoichiometry. Due to the high methyl acetate: oil molar ratio, the reverse reaction in Scheme 1 can be minimized and the concentration of methyl acetate can be considered as invariant. So, the overall interesterification has been assumed to follow a second-order reaction, which is also reported in the literature [20,21]. The governing rate equation may be expressed as:

$$-\frac{dC_{TG}}{dt} = r_{TG} = k \cdot C_{TG}^2 \tag{1}$$

where C_{TG} is the molar concentration (mol L^{-1}) of the triglycerides, t is the reaction time (min), r_{TG} is the reaction rate of the triglycerides (mol L^{-1} min^{-1}) and k is the reaction rate constant (L mol^{-1} min^{-1}). Integration of the above equation yields:

$$\frac{1}{C_{TG}} = k \cdot t + \frac{1}{C_{TG_0}} \tag{2}$$

Eq. (2) can be rearranged in terms of the conversion and can be expressed as follows:

$$\frac{X}{1-X} = C_{TG_0} \cdot k \cdot t \tag{3}$$

where C_{TG_0} is the initial triglyceride molar concentration (mol L^{-1}) and X is the conversion of triglyceride at any time t. The actual triglyceride concentration during the interesterification process can be calculated from the knowledge of the biodiesel yield and used to fit Eq. (2). A plot of $1/C_{TG}$ versus t will be a straight line if the model is valid, and k will be the value of the slope.

The Arrhenius equation gives a relationship between the specific reaction rate constant (k), absolute temperature (T) and the energy of activation (Ea) and can be given as follows:

$$k = A \exp\left[\frac{-Ea}{RT}\right] \tag{4}$$

where A is the frequency factor and R is the universal gas constant (J mol^{-1} K^{-1}). The equation can be rewritten as:

$$\ln(k) = \frac{-Ea}{RT} + \ln(A) \tag{5}$$

A plot of ln (k) vs. 1/T (the Arrhenius plot) gives slope equal to (−Ea/R) from which the activation energy can be determined.

3. Results and discussion

3.1. Effect of oil to methyl acetate molar ratio

In interesterification, as per the reaction stoichiometry, three moles of methyl acetate are needed for each mole of triglycerides, implying an OMAMR of 1:3. Interesterification reaction is a reversible reaction and to drive the reaction in forward direction usually an excess of methyl acetate is used as compared to the stoichiometric requirement. Considering this aspect, experiments were conducted with OMAMR ranging from 1:4 to 1:14 and the obtained results have been shown in Fig. 3. It has been observed that with an increase in the molar ratio from 1:4 to 1:12, the biodiesel yield increases from 45% to 90%. This is because as the interesterification reaction is reversible in nature, an excess of methyl acetate drives the interesterification reaction in the forward direction resulting in an increase in the conversion of WCO to biodiesel. It was also observed that further increase in the OMAMR from 1:12 to 1:14, did not result in any significant increase in the conversion of oil to biodiesel. The obtained results can be attributed to the fact that the use of higher molar ratio results in diluted products of biodiesel and triacetin which might initiate the reverse reaction to reduce the conversion [3].

The yield of biodiesel obtained (90%) at OMAMR of 1:12 was higher than that obtained under the conventional approach (76.7%) as reported by Casas et al. [6]. It is also interesting to know that the OMAMR used for this conventional approach is significantly higher at 1: 50. In the present study, higher yield of 90% is obtained at significantly lower excess of methyl acetate, which can be attributed to the cavitational events releasing large magnitude of energy due to the violent collapse of the cavities. Cavitation occurs at millions of locations in the reactor simultaneously and generates conditions of very high local temperatures and pressures (few thousand atmosphere pressure and few thousands

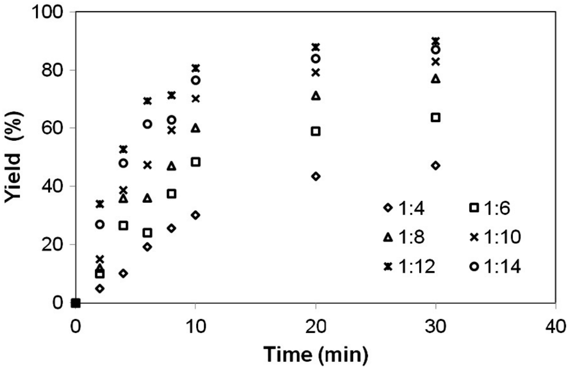


Fig. 3. Effect of oil to methyl acetate molar ratio on the yield of biodiesel. [Reaction conditions: Catalyst concentration = 1.00% (weight); Temperature = 40 °C; Percentage amplitude = 60%].

Kelvin temperature) with bulk ambient conditions. These cavitational effects are mainly responsible for the intensification of physical and chemical processing applications limited by mass transfer [22]. Considering the specific case of biodiesel synthesis, it can be said that the physical effects in terms of intense turbulence, liquid micro-circulation (acoustic streaming) and micro-emulsion formation giving enhanced areas for reaction, play a dominating role in intensification. Usai et al. [8] also carried out interesterification reaction of methyl acetate with triglycerides such as olive oils resulting into the formation of corresponding fatty acid methyl esters and triacetyl glycerol (triacetin). The reaction was catalyzed by lipase enzyme and effect of operating parameters such as type of catalyst, enzyme hydration and immobilization support has been investigated. It was reported that by using the immobilized lipase *Candida antarctica*, yields as high as 80% of both fatty acid esters and triacetin can be achieved at OMAMR of 1:20. Similarly, Xu et al. [9] obtained a FAME yield of 67% at 40 °C from refined soybean oil during interesterification reaction carried out at atmospheric pressure, with an OMAMR of 1:12 and a reaction time of 36 h using Novozym enzyme (0.1 g of enzyme per 1 g of oil). A major drawback of the use of the enzymes as catalysts is the long reaction times needed for high conversions as observed in the work of Xu et al. [9]. Campanelli [12] used methyl acetate instead of methanol for supercritical synthesis of glycerol-free biodiesel from edible oils (soybean and sunflower seed oil) and non-edible oils (*Jatropha curcas*) with different fatty acid composition and the supercritical process was also applied to waste oil with higher free fatty acid content. Experiments were carried out to investigate the influence of temperature, pressure and molar ratio of reactants on the conversion and it has been reported that the oil composition does not significantly influence the biodiesel yield. All the oils gave complete conversion after 50 min of experiment at 345 °C and 20 MPa pressure with oil: methyl acetate molar ratio equal to 1:42. It is observed that significantly higher molar ratios of the reactants and conditions of high pressure/temperature are usually required in supercritical methyl acetate interesterification reaction to shift the equilibrium in the forward direction.

A detailed comparison with literature indicates that as per the results obtained in the present work, WCO can be considered a potential good feedstock for the biodiesel manufacture. Use of ultrasound during the interesterification reaction reduces the requirement of methyl acetate and also requires considerably lower treatment times as well as milder ambient conditions, which should strongly influence the energy requirement for the overall synthesis process.

3.2. Effect of catalyst concentration

The effect of catalyst i.e. potassium methoxide concentration on the interesterification reaction of WCO has been investigated over a concentration range of 0.5% to 1.25% (by weight based on the weight of WCO). The obtained results have been depicted in Fig. 4. It can be seen from the figure that an increase in the catalyst concentration from 0.5% to 1% results in an increase in the biodiesel yield from 45% to 90%. Initially, an insufficient amount of potassium methoxide (0.5%) results in incomplete conversion of triglycerides into the corresponding methyl esters i.e. biodiesel, as indicated from its lower ester content. However, a further increase in the catalyst concentration from 1 to 1.25 wt.% does not show a significant increase in the biodiesel yield. Suppalakpanya et al. [23] reported similar results for transesterification reaction of crude palm oil where an addition of excess amount of catalyst (potassium hydroxide) gave rise to the formation of an emulsion which in turn led to the formation of gels and a decreased percentage of ethyl ester content in the final mixture. Formation of gel hinders the glycerol separation from the mixture and hence reduces the obtained ester yield. The optimum amount of catalyst required in the present case was established at 1 wt.% level, which is based on the fact that a further increase in the catalyst concentration will not increase the conversion and will lead to expensive catalyst recovery costs. Casas et al. [24] carried out interesterification reaction between refined sunflower oil and methyl acetate for biodiesel production at different catalyst ratio (0.1:1, 0.15:1 and 0.2:1) and it was reported that a maximum conversion of 76.7% was obtained at optimized catalyst to oil molar ratio of 0.2:1 (i.e. 1.04% by weight of the catalyst).

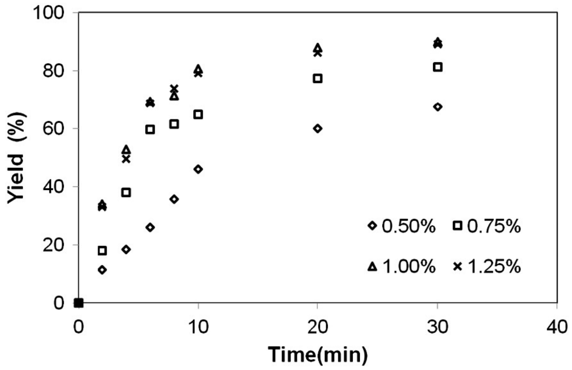


Fig. 4. Effect of catalyst concentration on the yield of biodiesel. [Reaction conditions: OMAMR = 1:12; Temperature = 40 °C; Percentage amplitude = 60%].

3.3. Effect of temperature

The effect of operating temperature on the yield of biodiesel from WCO in interesterification reaction has been investigated over a temperature range from 30 to 50 °C under the fixed conditions of reactant molar ratio and catalyst loading (1:12 of OMAMR and 1 wt.% catalyst concentration). The obtained results have been presented in Fig. 5 which indicate that with an increase in temperature from 30 to 40 °C, a corresponding increase in the biodiesel yield from 78 to 88% is obtained and a further increase in the reaction temperature from 40 to 50 °C results only in a marginal increase in the biodiesel yield from 88 to 93%. The obtained results can be explained on the basis of an enhanced solubility of methyl acetate in the other phase due to increase in the reaction temperature resulting into better contact of the reactants leading to higher yield of biodiesel from WCO. Any further increase in the temperature has no detectable effect on the final conversion to ester which can be also attributed to lower extent of cavitational effects at higher operating temperatures. Thus, an optimum temperature for efficient processing exists. It is also important to note here that higher temperatures also decrease the time required to reach the maximum conversion. Casas et al. [24] reported similar results for interesterification of sunflower oil with methyl acetate for biodiesel and triacetin production over the operating temperature range from 30 to 50 °C. Tan et al. [3] also reported that the yield of biodiesel increased with an increase in the temperature from 340 to 420 °C at a pressure of 220 bar in the case of supercritical interesterification reaction of purified palm oil. The observed results have been explained on the basis of enhanced reactivity between methyl

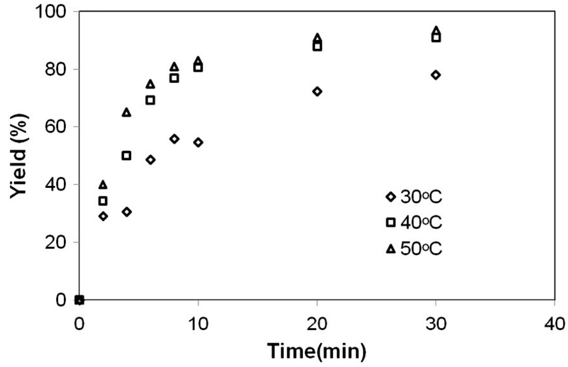


Fig. 5. Effect of temperature on the yield of biodiesel. [Reaction conditions: OMAMR = 1:12; Catalyst concentration = 1.00% (weight); Percentage amplitude = 60%].

acetate and triglycerides which leads to a rapid reaction rate. Beyond the optimum temperature, the yield remained constant as the high temperature had an adverse effect on the FAME which has relatively low thermal stability at extreme conditions. Campanelli et al. [12] reported that the yield of FAME declined in the case of prolonged interesterification reaction at 345 °C possibly attributed to the thermal decomposition of the FAME (especially the polyunsaturated ones) occurring beyond an operating temperature of 300 °C. Similarly, Saka el al. [14] reported less yield of FAME at 380 °C compared with 350 °C due to the breakdown of unsaturated fatty acids at the higher temperature. Thus, it is very important that an optimum operating temperature is selected and comparison of the literature has also confirmed that similar conversions have been obtained at much lower operating temperatures in the case of ultrasound assisted synthesis process.

3.4. Effect of percentage amplitude of ultrasound

The variation in the percentage amplitude of ultrasonic horn decides the ultrasonic power input into the system and hence it is also an important influencing factor for the degree of intensification of interesterification reactions. The power input to the system decides the extent of cavitational activity in the reactor and hence the extent of biodiesel yields. The effect of percentage amplitude of ultrasonic horn on the yield of biodiesel from WCO has been studied at different values such as 40, 50, 60 and 70% corresponding to 300, 375, 450 and 525 W respectively. The obtained experimental data has been presented in Fig. 6. It can be seen from the figure that the biodiesel yield increases from 68 to 90% with an increase in the percentage amplitude of ultrasonic horn from 40 to 60% (actual power from 300 to 450 W) and no significant change is observed for a further increase in the percentage amplitude to 70% (actual power of 525 W). The obtained results can be attributed to enhanced cavitational effects due to an increase in the percentage amplitude. Higher degree of cavitational effects also ensures sufficient mixing and emulsification of two immiscible reaction layers. Beyond the optimum percentage amplitude, the yield slightly decreased from 90 to 88%, which can be attributed to the fact that at very high amplitudes, higher extents of cavitation events can result in cushioning of the cavity collapse which results in decreased energy transfer into the system giving lower cavitational activity and hence biodiesel yields. Calorimetric study has been carried out with fixed amount of methyl acetate (50 ml) measuring the time required to increase the temperature by 15 °C. The energy transfer efficiency has been calculated based on the input energy (percentage amplitude × rated power) and actual energy dissipation (m × Cp × ΔT) into the methyl acetate solution. The obtained results for the different percentage amplitude from 30 to 90% are shown in Fig. 7. From Fig. 7, it can be established that maximum energy transfer efficiency is obtained at percentage amplitude equal to 60%.

Chand et al. [25] have also reported similar results for biodiesel production from soybean oil using ultrasonic irradiations. Experiments carried out at three levels of amplitude (60, 120, and 180 μ_{mpp}) in pulse mode (5 s on/25 s off) indicated that highest yield was obtained with 120 μ_{mpp} amplitude. It has been reported that at the higher amplitude of 180 μ_{mpp}, excessive cavitation or fine bubble formation occurs at the interface between the horn and the liquid, resulting in the formation of an intense near-field cavitation region near the horn. Suslick and Nyborg [26] describe such near-fields as having high attenuation, thus inhibiting penetration of sound waves throughout the reaction mixture, which may be responsible for lowering the product yield at higher power dissipations beyond the optimum value. Mahamuni et al. [27] have also observed similar effects of power on biodiesel yield in the presence of ultrasound. It has been reported that the biodiesel yield increased to 92.5% in 30 min with an initial increase in the ultrasonic power from 46 to 143 W. Kumar et al. [28] investigated the effect of ultrasonic amplitude on the enzymatic transesterification of *Jatropha curcas* oil for biodiesel production at four levels of 30, 40, 50 and 60%. It has been reported that a maximum of 84% conversion was obtained at an ultrasound amplitude of 50% (i.e. 375 W) using a molar ratio of oil to methanol as 1:4 catalyst concentration as 5 wt.% of oil, and reaction time of 30 min. Ji et al. [29] studied the effect of ultrasonic power on biodiesel yield at three levels of 100, 150, and 200 W and found that optimum conversion of 100% was obtained at the intermediate power level of 150 W using the 1:6 molar ratio of soybean oil/methanol in the presence of base catalyst at 45 °C.

3.5. Reaction kinetics

Time history of biodiesel yield from triglycerides in the reaction mixture at different temperatures has been shown in Fig. 5 for alcohol to oil molar ratio of 1:12, catalyst concentration of 1% and percentage amplitude of 60% (i.e. 450 W). The obtained data for the conversion with time have been analyzed using a second-order kinetic model to determine the rate constants at different temperatures. The consideration of irreversibility of this reaction is favored with an excess of methyl acetate that induces low concentrations of triglycerides in the equilibrium composition, similar to an irreversible reaction. Fig. 8 shows these plots of X/(1-X) vs. time at different reaction temperatures of 30, 40 and 50 °C and the obtained rate constants from these plots have been given in Table 2. It has been observed that the rate constant for interesterification reaction increased from 0.22 to 0.93 L/(mol min) with an increase in the temperature from 30 to 50 °C. Similar results in terms of second-order kinetic fitting has been reported by Casas et al. [24] for interesterification of sunflower oil at different temperatures. Musavi et al. [30] also observed that rate constant increased with an

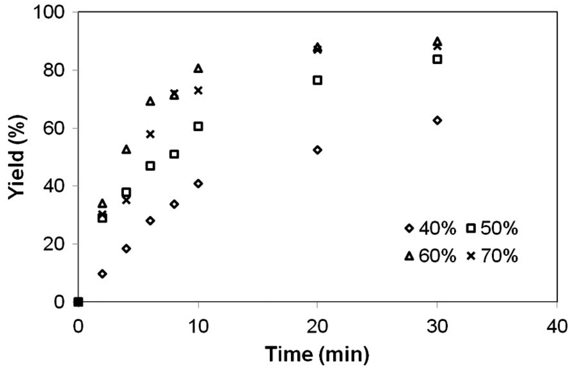


Fig. 6. Effect of percentage amplitude of ultrasound on the yield of biodiesel. [Reaction conditions: OMAMR = 1:12; Catalyst concentration = 1.00% (weight); Temperature = 40 °C].

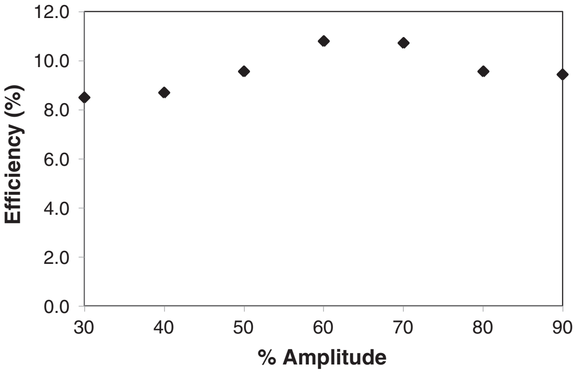


Fig. 7. Calorimetric study for finding the energy efficiency at different amplitudes.

increase in the temperature of interesterification reaction of soybean oil over the temperature range of 10–80 °C. The reaction rate for biodiesel synthesis is also increased due to enhanced interfacial area between oil and methyl acetate phase, due to cavitational effects, mainly in terms of the intense levels of turbulence and mixing generated in the reactor. The physical effects contribute to intensification because of the generation of microemulsions between the two phases taking part in the reaction, and hence the available interfacial area between the reactants increases enormously, giving faster reaction rates and the requirement of less-severe conditions, in terms of the operating temperature [31].

The activation energy was also obtained using rate constant data for the controlled temperature experiments at 30, 40, and 50 °C. The obtained result is shown in Fig. 9, with the activation energy calculated to be 58.170 kJ/mol and the pre-exponential factor found to be 2.67×10^9 L/(mol min). These values of activation energy for interesterification of WCO using ultrasound are in the same range as those reported by Casas et al. [24] in the study of kinetics of sunflower oil interesterification. The value of activation energies ranged from 24.318 to 88.551 kJ/mol for the sunflower oil interesterification. The resulting Arrhenius expression for biodiesel synthesis using ultrasound based on current work is given by

$$k = 2.67 \times 10^9 \cdot e^{\left(\frac{-58.170}{RT}\right)}$$

Mahamuni and Adewuyi [27] carried out transesterification of soybean oil using high frequency ultrasound and reported that ultrasonication provides an effective way to attain the required mixing while providing the necessary activation energy. Campanelli et al. [12] synthesized biodiesel from edible, non-edible and waste cooking oils via supercritical methyl acetate transesterification and reported that activation energies depend on the vegetable oil and the employed supercritical alcohol; a value of 56 kJ/mol was found for supercritical methanol transesterification of soybean oil over the temperature range of 240 to 280 °C at 28 MPa, with oil: methanol molar ratio equal to 1:42. It was also reported that apparent activation energies for the supercritical methyl acetate process are higher showing a lower reactivity of this solvent compared to methanol.

3.6. Biodiesel properties

Biodiesel properties i.e. density, flash point, kinematic viscosity, and acid value of the final dried product obtained using both methods i.e. conventional as well as ultrasound assisted synthesis are given in the Table 3. It is observed that the properties of biodiesel obtained by both methods match with the ASTM D 6751 standards. The flash point is one of the key parameters for biodiesel, which indicate the working feasibility and engine performance and depends on the quality of separation of the unreacted triglyceride from the final product, fatty acid methyl esters and triacetin. The flash point of the biodiesel synthesized from ultrasound (155 °C) has been found to be lower than that obtained using the conventional method (190 °C) which can be attributed to higher purity of the final product. Flash point of biodiesel obtained in the present study is also less as compared to biodiesel produced from other sources (Karanja (230 °C) [32] and *Madhuca indica* (208 °C) [33]). Based on these properties, the superiority of the ultrasound assisted synthesis can be clearly established.

Table 2
Reaction rate constant and activation energy of interesterification reaction.

Temperature (°C)	Rate constant (k) (L/mol min)	Correlation factor R^2	Activation Energy (J/mol)
30	0.22	0.987	58,170
40	0.66	0.978	
50	0.93	0.998	

4. Comparison of acoustic cavitation with conventional stirring

The optimized parameters for the interesterification of waste cooking oil have been established as OMAMR of 1:12, catalyst concentration of 1% and temperature of 40 °C. The comparison of the obtained results using conventional method and ultrasound assisted technique under these optimized conditions has been presented in Fig. 10. It can be seen that the biodiesel yield is higher for ultrasonic technique (90%) as compared to conventional method (70%). The obtained superiority of ultrasound assisted approach can also be confirmed from literature illustrations. Casas et al. [6] carried out interesterification of sunflower oil using conventional approach and reported maximum biodiesel yield of 76.7% under conditions of molar ratio of 1:50 and, catalyst to oil molar ratio 0.2 (~1.04 wt.%) at 50 °C. The current work has shown much higher conversions for the interesterification reaction at much lower excess of reactants which also should reduce the separation loads. The higher conversion obtained due to the use of ultrasonic irradiations is attributed to the physical effects of the cavitation phenomena. It is important to note here that only the physical effects in terms of intense turbulence and microstreaming generated during the cavitation plays a dominating role in intensification. The higher biodiesel production obtained using ultrasonic irradiations is due to local turbulence, liquid micro-circulation (acoustic streaming) and micro-emulsion formation giving enhanced areas for reaction. Because of the generation of microemulsions between the two phases taking part in the reaction, the available interfacial area between the reactants increases enormously, giving faster reaction rates and the requirement of less-severe conditions, in terms of the operating temperature and also lowering the degree of excess reactants for similar yields.

Similar superiority of use of ultrasound has been observed in the literature for the transesterification reactions though not much illustrations can be obtained for the interesterification reaction. A few

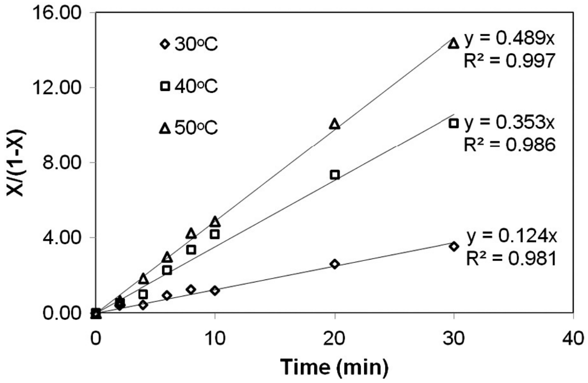


Fig. 8. Kinetic study for establishing the rate constants.

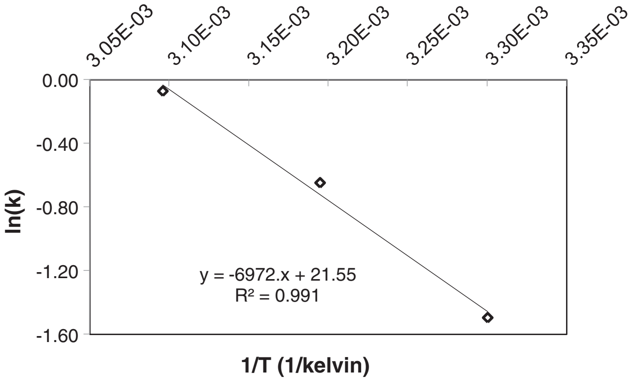


Fig. 9. Arrhenius plot for estimation of activation energy.

Table 3
Biodiesel properties.

Property	Conventional	Ultrasound	ASTM D6751
Density, g/cm^3	0.8637	0.871	0.86–0.9
Kinematic viscosity, 40 °C, mm^2/s	3.64	3.78	1.9–6.0
Flash point, °C	190	155	130 min
Acid value, mg of KOH/g of oil	0.71	0.28	0.5 max

illustrative examples have been discussed here just to give some degree of confidence for the use of ultrasound based synthesis approach. Babajide et al. [34] conducted transesterification of waste cooking oil using ultrasonic homogenizer with 20 kHz frequency and power output of 400 W at different catalyst loadings and reaction times. It has been reported that ultrasonic homogenization proved suitable for large-scale processing of waste cooking oils resulting in a better yield of 90% and higher conversion efficiency of 98%. The effective mass transfer in the ultrasonic field enhanced the rate of transesterification reaction compared to mechanical mixing (stirring conditions). Hingu et al. [35] investigated the transesterification of used frying oil using low-frequency ultrasonic reactor (20 kHz) and conventional stirring approach based on the use of a six-blade turbine with diameter of 1.5 cm operating at 1000 rpm. It has been reported that acoustic cavitation results in 89.5% conversion whereas the conventional stirring method results in much lower extent of conversion (57.5%) over similar time of operation as 40 min. The obtained results have been attributed to the fact that as the reaction is mass transfer controlled, the micro-level turbulence generated due to the oscillation and collapse of cavitational bubbles results into the higher interfacial area and hence higher conversion.

Another advantage offered by the use of the ultrasound approach is in terms of the requirement of lower excess of methyl acetate (lower molar ratios) for achieving a similar or higher level of conversions. A lower requirement of excess methyl acetate will certainly reduce the energy requirements for the overall process, because methyl acetate separation using distillation is a significantly energy-intensive operation, controlling the overall economics of the biodiesel synthesis process. The ultrasound-based process also offers easy purification of the product and the final product properties are more suitable, compared to the conventional approach as shown in Table 3. The energy requirement for conventional method and ultrasonic technique is 22,154 and 4780 kJ/kg respectively. The overall production costs of the fatty acid methyl esters depend strongly on the total energy requirement for the process in addition to the cost of raw materials. Use of sustainable feed stock in terms of WCO indeed gives an advantage and the use of ultrasonic technique also gives additional advantage in terms of the lower energy requirements and operations at ambient conditions.

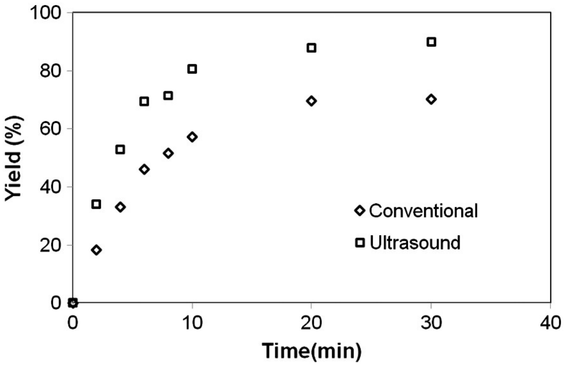


Fig. 10. Comparison of biodiesel yield in the ultrasound assisted and conventional methods. [Reaction conditions: Molar ratio (OMAMR) = 1:12; Catalyst concentration = 1.00% (by weight); Temperature = 40 °C; Ultrasound method: Percentage amplitude = 60%; Conventional method: stirrer speed = 1000 rpm].

5. Conclusions

The present work has established the utility of ultrasound assisted interesterification process for the production of biodiesel and triacetin from WCO. The process can be a useful alternative to the more commonly used transesterification as it generates triacetin instead of glycerol which is an important additive to improve the properties of biodiesel particularly in cold conditions. The presented results are very important in the current context as it has focused on one of the cheaper synthesis routes for biodiesel production based on the use of waste oils with significant degree of intensification using ultrasound. Higher biodiesel yield has been observed in the case of ultrasonic technique as compared to the conventional method and also the properties of the synthesized biodiesel are better. The excess of reactants required is also lower as compared to the conventional routes and supercritical oxidation route which gives benefits in terms of lower separations costs. The work has confirmed for the first time that significant process intensification is obtained for the synthesis of biodiesel based on the interesterification approach. To summarize, the main advantages offered due to the use of sonochemical reactors, as revealed by optimization studies related to the various operating parameters such as molar ratio, catalyst concentration, and reaction temperature, are a reduced reaction temperature (savings in the energy required for heating of the process streams), a lower reaction time (energy savings in reactor), and the requirement of a smaller amount of excess methyl acetate for equivalent levels of equilibrium conversion (considerable energy savings in the separation units). The kinetics of the conversion of triglycerides through interesterification follows a second-order reaction scheme and it was observed that the rate constant increased with an increase in the operating temperature. The properties of biodiesel produced from both methods match the ASTM standards with superior properties for the ultrasound assisted approach. Overall, it can be said that use of ultrasonic irradiations considerably enhances the rates of biodiesel synthesis and would also lead to a substantial energy savings, because of various process improvements such as use of lower temperature and lower excess of reactants, as observed in the present work.

Acknowledgment

GLM is thankful to the University Grants Commission, Government of India for the financial assistance. GLM would also like to acknowledge the help of B.N. Rekha in the preparation of the manuscript.

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