Research paper

Production and purification of biodiesel produced from used frying oil using hydrodynamic cavitation

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ABSTRACT

This work describes the biodiesel production from used frying oil using a hydrodynamic cavitation reactor as well as separation and purification of fatty acid methyl esters (FAME). Under the optimized process conditions, i.e., methanol to oil molar ratio of 4.5:1 and catalyst (KOH) concentration of 0.55 wt%, the conversion achieved was 93.86 mol%. Higher conversion (93.6%) was obtained in only 20 min as compared to 88.5% in 1 h in stirred tank reactor. Due to the completion of transesterification reaction, the amount of intermediate diglycerides and monoglycerides present in the reaction mixture was less. It helps for the complete separation of methyl ester and glycerol layers without hindrance in 1 h. Small amount KOH catalyst used for completion of reaction reduces amount of KOH and soap in ester layer which further helps to form a less stable emulsion during water washing step. The complete separation was observed at 70 °C temperature in just 3 h. Thus, this study indicates that the increased production capacity can be achieved by shortening the time for the separation and purification.

1. Introduction

Biodiesel has got a tremendous potential as a fuel and has the potential to reduce the amount of CO, particulate matter, and GHG (greenhouse gas) emissions [1]. Hence, there is a considerable interest in exploring and developing the use of biodiesel fuel. However, the major barrier in the commercialization of biodiesel production from vegetable oils is its high feedstock cost, if virgin vegetable oil is used [2]. The cost of vegetable oil has a crucial role in the economics of the biodiesel. Thus, developing countries cannot afford to utilize edible vegetable oil as a raw material for biodiesel production. Used frying oil is much less expensive than pure vegetable oil, and might reduce the biodiesel production cost up to 60–70% [3]. India produces around 9.2 million tons of waste cooking oil per annum, which is highest in the world [4]. Kabir et al. reported that average WCO generated in Malaysia per household is 2.34 kg/month [5]. The studies conducted by Mittelbach and Enzelsberger [6] on frying oil suggest that, during frying, basically thermolytic, oxidative, and hydrolytic reactions occur. Due to these reactions along with methyl esters, dimeric fatty acid methyl esters are also formed. However, in the same study it was revealed that,

dimeric and polymeric methyl esters had no negative influence on engine performance of city buses, in long-term performance tests done with 100% ester from frying oil. Hence, use of used frying oil has been selected as a basic raw material for biodiesel production.

The nonpolar methyl group of methanol is too small to interact with the oil, which causes limited solubility of the two phases in transesterification reaction. Thus, the methanolysis mixture consists of two phases, as the nonpolar (mostly triglycerides) phase and polar (mostly alcohol) phase are immiscible. The catalyst is located only in the methanol phase, and the minuscule concentration of oil in that phase limits the reaction [7]. The transesterification of used frying oil can be performed using alkaline, acidic or enzymatic catalysts. Depending on the undesirable compounds (especially FFA and water), each catalyst has its own advantages and disadvantages. Enzyme-catalyzed procedures, using lipase as catalyst found, that this route does not produce side reactions [8,9]. However, the lipases are very expensive for industrial scale production [10] and the rate of transesterification reaction is also very slow. Acid-catalyzed process is useful when a high amount of free fatty acids are present in the vegetable oil, but the reaction time is very long. In the base-catalyzed procedure, some soap is formed as a result of the presence of free fatty acids and acts as an emulsifier, which helps mixing of the reactants. However, it is necessary to control the amount of alkali catalyst because the excess alkali enhances the saponification reaction which reduces the yield of

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product [11]. Also, the excess of soap forms emulsion during washing step which causes difficulty in separation and purification [12].

Consequently, another approach which leads to reduction in the operating cost is the improvement in the technology. Work has been carried out on the transesterification of used frying oil by conventional stirred tank reactor. The molar ratio of methanol to oil, catalyst concentration, reaction temperature and reaction time are the main factors affecting the reaction cost. If catalyst concentration exceeds the optimum value, the conversion increases but gives emulsions because of the formation of soap in washing step, thus hindering the purification and reducing product yield. Similarly, reaction remains incomplete for the molar ratio of methanol to oil less than optimum value and if operated beyond the optimal ratio, both the ester content and the product yield are not increased but results in additional cost of methanol recovery [12]. The higher amount of methanol and alkali catalyst causes troubles in separation and ultimately reduces the product yield. To address these issues, Hingu and Rathod [13] have studied the synthesis of biodiesel from used frying oil using sonochemical reactors. In their work, it has been illustrated that the role of ultrasonic field in inducing an effective emulsification and mass transfer was important and the rate of ester formation was significantly enhanced. However, the scale up is the major hurdle with sonochemical reactors. Therefore it was still essential to optimize the transesterification process with a potential technology which can give a high rate of reaction with high yield of the esters. Hydrodynamic cavitation requires mild reaction conditions to carry out reactions. It is one of the energy efficient, simple and cheapest methods of generating cavitation, and also scale up of this process is relatively easy [14]. The production of biodiesel using hydrodynamic cavitation has been reported earlier [15–17]. In earlier work, transesterification of used frying oil has been carried out in a hydrodynamic reactor [17]. However, this study reports only the optimization of geometrical parameters such as diameter and number of holes, free area etc. at constant methanol to oil ratio and KOH concentration. Thus, there is indeed need to study the effect of these parameters (methanol to oil ration and KOH concentration) in hydrodynamic cavitation reactor for the transesterification of used frying oil.

Thus, the aim of this paper was to optimize above mentioned parameters in a hydrodynamic cavitation reactor with waste frying oil as feedstock which might be proved as a more efficient alternative for biodiesel production.

Apart from the transesterification reaction, the actual process of biodiesel production includes many sub process steps such as product separation and purification which are important as these steps also decide the cost of the process. After the reaction, the glycerol is removed from the methyl esters. Due to the low solubility of glycerol in the esters, this separation generally occurs quickly and may be accomplished with either a settling tank or a centrifuge. The excess methanol reduces the separation of ester and glycerol phases due to the reduced density of former phase. Hence, an additional objective of the present work was to study the effect of different molar ratio of methanol to oil on the separation of ester (product) and glycerol (byproduct) layer. However, this excess methanol is usually not removed from the reaction stream until and after the glycerol and methyl esters are separated due to concern about reversing the transesterification reaction. Water may be added to the reaction mixture after the completion of transesterification to improve the separation of glycerol by removal of the alkali catalyst, soap and trace amount of glycerol and methanol to get a good quality biodiesel fuel [18]. But, it has been reported that, this washing step takes a substantial time to separate the clean ester phase from the water containing impurities. This problem can be solved by breaking an emulsion formed during washing step at high temperature. Therefore, in washing step, the effect of

Table 1
Properties and composition of UFO.

Properties and FA compositon of WCO	Value
Saponification value (mg of KOH/g of oil)	202.4
Acid value (mg of KOH/g of oil)	2.41
Water content (%)	0.5
Density (g/cm³)	0.920
Linoleic acid (%)	61.89
Oleic acid (%)	33.06
Palmitic acid (%)	3.27
Stearic acid (%)	1.78

temperature on time required for phase separation by gravity settling has also been studied.

2. Materials and methods

2.1. Materials

Used frying oil (sunflower oil) was obtained from Garnish restaurant, Kings Circle, Mumbai, India. It consists of 95% unsaturated fatty acids and only 5% saturated fatty acids as shown in the Table 1. During the frying of vegetable foods, this sunflower oil was heated at around 180–190 °C for around 5–6 h Methanol (99%), potassium hydroxide pellets (LR grade), anhydrous sodium sulphate (AR grade), sulfuric acid (98%) used in the experimental work were purchased from S.D Fine-Chem. Ltd, Mumbai, India. HPLC grade Acetonitrile and acetone solvents for analysis on HPLC were purchased from G. Kuntal Implements, Mumbai. The standards such as methyl linoleate, methyl oleate, and methyl stearate were procured from sigma-Aldrich.

2.2. Analytical method

The Samples collected were analyzed using high performance liquid chromatography (HPLC) with UV-8010 detector at a wavelength of 210 nm [17]. A C18 (JT Baker) octadecyl 5 μm, length 4.6 mm × 250 mm column and the mobile phase (mixture of acetonitrile and acetone in the proportion of 95:5) at 0.8 mL/min flow rate was used. The composition of used frying oil (sunflower oil) was obtained and compared with the literature [17]. Molecular weight is derived from the molecular weight of the triglycerides corresponding to the FAME from biodiesel following Equation:

$$P_m = \Sigma P_{mi} \times X_i$$

where, P_m is the used frying oil molecular weight, P_{mi} is the molecular weight of triglycerides from FAME and X_i is the percent of FAME.

$$\text{Conversion (\%)} = \frac{\frac{P_b}{P_{mb}} \times \text{biodiesel content \%}}{\frac{P_a}{P_{ma}} \times 3}$$

where, P_b is the weight of biodiesel, P_{mb} is the molecular weight of biodiesel, and biodiesel content % is the FAME content of biodiesel, P_a is the weight of used frying oil in the transesterification and P_{ma} is the used frying oil molecular weight of oil [19].

2.3. Experimental method

2.3.1. Experimental set-up of hydrodynamic cavitation reactor

As shown in the Fig. 1, the hydrodynamic cavitation reactor consists of a collecting tank with 10 L capacity which was connected to the multi-stage, vertical high-pressure centrifugal pump having electric power rating of 1.75 kW. The pipe connected to the discharge side of the pump branches into main line and bypass line and both lines were again recycled to the collecting tank. The
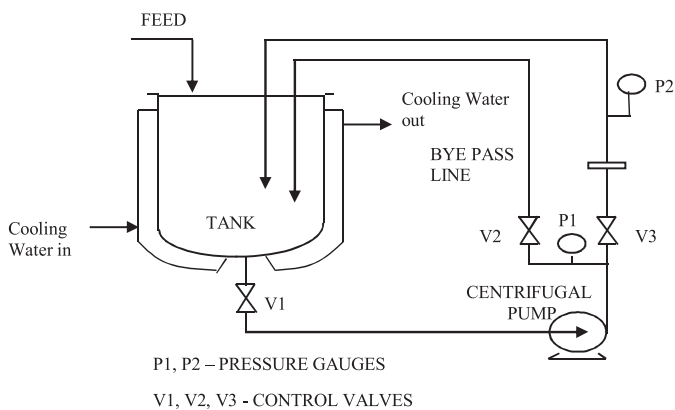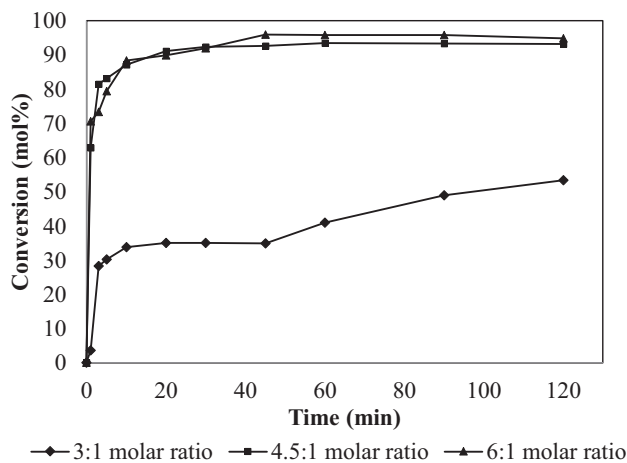
Fig. 2. Effect of methanol to oil molar ratio on % oil conversion.

orifice plate incorporated for cavitation had 16 holes of 3 mm diameter (i.e. total free area of 113 mm^2). The pressure in the main line and bypass line was adjusted by throttling valves and pressure gauges. The sample ports were connected to the main line as well as bypass line.

2.3.2. Experimental procedure for hydrodynamic cavitation reactor

The hydrodynamic cavitation reactor was fed with 6420 g of used frying oil. Potassium hydroxide used as catalyst on wt % basis of oil was mixed with known quantity of methanol and added to the reactor [17]. The methanol quantity was taken as per the different molar ratio of alcohol to oil (i.e. 1410 g for 6:1 molar ratio, 1060 g for 4.5:1 molar ratio and 705 g for 3:1 molar ratio). An excess amount of methanol was used to take care of the reversible reaction. To optimize the catalyst concentration, the reactions were carried out separately using two different KOH concentrations i.e., 0.55 and 1% KOH with optimized quantity of methanol. The reaction mixture was circulated through the cavitation zone of the reactor for longer time i.e. 2 h The temperature achieved by cavitation and circulation effect was around 45 °C. The samples were taken after every 1, 3, 5, 10, 20, 30, 45, 60, 90 and 120 min. In order to quench the reaction each sample was taken in a vial containing 30% H$_2$SO$_4$ solution in water. The organic (mainly methyl ester) layer and the aqueous (glycerol) layer were separated and the excess methanol was removed from the methyl ester layer with rotary evaporator. The product mixture was diluted and analyzed by HPLC.

2.3.3. Experimental set-up for stirred tank reactor

The reaction run with the optimized process parameters was carried out in a conventional stirred tank reactor to compare the performance of the hydrodynamic cavitation reactor. The three-neck borosilicate reactor of 80 mm internal diameter and 500 mL volume provided with a six bladed (pitched blade) glass turbine was used. The reactor was placed in a constant temperature oil bath. The reaction temperature was maintained by using temperature controller. The reactor was also equipped with a condenser to reduce the losses of methanol due to evaporation. The stirring at 1000 rpm was provided by means of an electric motor having provision for speed control.

2.3.4. Experimental procedure for stirred tank reactor

In a stirred tank reactor, 183 g of used frying oil was charged along with 1 g of KOH (0.55 wt% of oil) in 30 g of methanol (4.5:1 molar ratio methanol to oil). The transesterification reaction was carried out at constant temperature of 45 °C at 1000 rpm. The product mixture was diluted and sample was analyzed by HPLC.

2.3.5. Experimental procedure for separation study of methyl ester and glycerol layers at different methanol to oil molar ratio

The reaction mixtures of different ratios were taken in the measuring cylinders. The level of the interface of both layers was noted at different time intervals. Also, the sample of the methyl ester layer was taken out from 0.5 cm above the interface layer at fixed time intervals and the ester content was measured by HPLC analysis to confirm the complete separation of both layers.

2.3.6. Experimental procedure for the separation study of washing step at different temperatures

The effect of temperature on phase separation time and degree of separation during the washing step of methyl ester was studied. The different temperatures preferred were 30 °C, 50 °C and 70 °C. Ester layer from the same reaction mixture was taken in the equal quantity and two volume of water was added to these ester layers. The mixture was kept for settling at above mentioned temperatures in three separate measuring cylinders of same size. The interface height of both layers was noted down at different time intervals. Also, the methyl ester layer was taken out from 0.5 cm above the interface layer and the ester content was measured by HPLC analysis to confirm the complete separation of both layers.

In order to check the reproducibility, all the above experiments have been performed two times and the average values have been reported here.

3. Results and discussion

3.1. Effect of methanol to oil molar ratio

Methanol to oil molar ratio is one of the influential variables on transesterification reaction rate, oil conversion and product yield. Experiments were conducted with different methanol to oil molar ratios of 3:1, 4.5:1 and 6:1 and results are shown in Fig. 2. For all three sets of experiments, the catalyst (KOH) concentration was kept 1 wt% of oil. Due to the cavitation effect, the temperature of the reaction mixture was reached to 45 °C. Fig. 2 shows that the conversion obtained at a molar ratio of 3:1 was less (54%) as compared to higher ratios of 4.5:1 and 6:1 (i.e 93.86% and 95.4% respectively). Although, three moles of methanol react with one mole of triglyceride to yield three moles of fatty acid methyl esters and one mole of glycerol based on stoichiometry, the transesterification being reversible reaction an excess of methanol is required to shift the equilibrium to product side. Also, addition of methanol reduces the viscosity of the reaction mixture and increases the cavitation phenomenon and thus the mass transfer, thereby maximize the
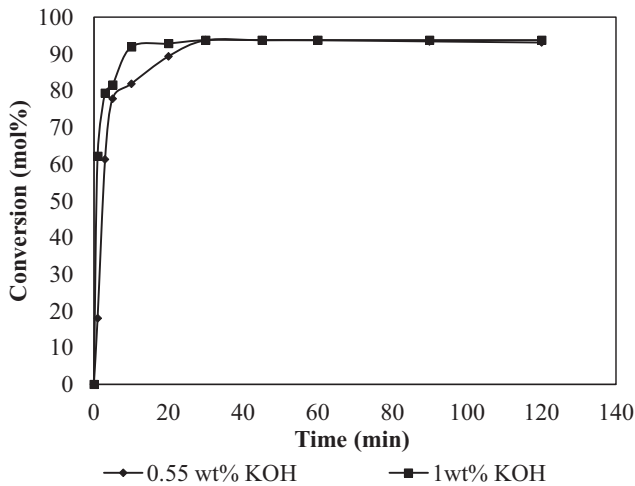
Fig. 3. Effect of catalyst (KOH) concentration on % oil conversion.

Fig. 4. Comparison of hydrodynamic cavitation reactor and stirred tank reactor.

conversion. Hence, the higher molar ratios than that of theoretical requirement resulted in a high conversion and ensured complete reaction. Because of high viscosity of used frying oil, the miscibility of oil is very less and the methanol requirement is usually greater than that for virgin vegetable oil [12]. However, it was observed that the cavitation effect causes emulsification of immiscible liquids i.e. triglycerides (non-polar phase) and methanol (polar phase) and the temperature was also elevated to 45 °C in hydrodynamic cavitation reactor, which has positive effect on reaction kinetics. Thus the quantity of methanol required for the completion of the reaction in hydrodynamic cavitation reactor was reduced. The difference in conversion obtained at 4.5:1 and 6:1 was marginal. Gole et al. [20] reported that cavitational activity increases the interfacial area of contact between the heterogeneous phases of the methanol and oil and thus increased rate of reaction. Many investigators have reported that high amount of methanol present in the reaction mixture also lowers the separation rate of ester and glycerol layer because of high solubility of glycerol as well as esters in methanol [21]. After completion of the transesterification reaction the excess amount of methanol present in the reaction mixture also increases the cost of methanol recovery. Thus the molar ratio of methanol to oil is an important parameter affecting the methyl ester yield and purity. Therefore, the methanol to oil molar ratio 4.5:1 was taken as the optimum ratio for the transesterification reaction of used frying oil in hydrodynamic cavitation reactor.

3.2. Effect of catalyst concentration

Fig. 3 shows the consequence of catalyst concentration on the transesterification of the used frying oil using hydrodynamic cavitation reactor investigated with different concentrations of 0.55 and 1 wt% KOH on the basis of oil. The optimized methanol to oil molar ratio of 4.5:1 was taken for both experimental runs. The operation conditions during the reaction process were maintained constant at reaction temperature of 45 °C and reaction time of 120 min. Experimental results from Fig. 3 shows that as the catalyst concentration increased from 0.55 to 1%, the initial rate of the conversion of triglyceride was also increased, but after 30 min the reaction rate and conversion of both the reactions were constant. It was revealed from the results that KOH concentration of 0.55 wt% was adequate to complete the conversion of triglycerides into methyl esters in hydrodynamic cavitation reactor.

In most of the previous work it was investigated that 1 wt% of KOH concentration was necessary for maximum conversion in conventional processes. In base-catalyzed procedure, some soap
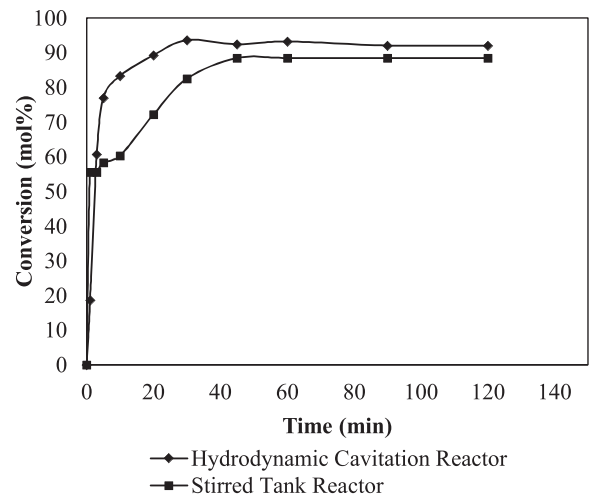
formed acts as phase transfer catalyst, thus helping the mixing of the triglycerides and methanol [22]. However, in hydrodynamic cavitation reactor small amount of KOH (i.e.0.55wt %) was sufficient for the completion of transesterification reaction as compared with conventional stirred tank reactor. This occurred due to the collapse of the cavitation bubbles which disrupts the phase boundary and causes emulsification that impinges one liquid to another and the mass transfer hurdle was compensated for progression of the reaction.

As the KOH concentration was increased from 0.55 to 1.0 wt%, a marginal change in the conversion of the methyl ester product was observed at initial time. Since the quantity of fatty acid present in used frying oil (present study) is less, the higher amount of catalyst did not show any effect on the conversion. So, excess KOH catalyst had no positive effect on the ester content and also added extra cost to the process for removing the excess catalyst and soaps at the post-treatment stage of ester purification. As a whole, the catalyst concentration has a large effect on the purity and yield of methyl ester obtained, and should be controlled accurately. Therefore, the catalyst concentration was taken as 0.55 wt% KOH on oil basis for the transesterification of used frying oil using hydrodynamic cavitation reactor.

3.3. Comparison of hydrodynamic cavitation reactor with stirred tank reactor

The performance of the hydrodynamic cavitation reactor was compared with the stirred tank reactor for alkali catalyzed transesterification reaction of used frying oil with methanol. The reaction run was carried out in the conventional stirred tank reactor. Used frying oil, methanol and KOH were taken in appropriate amounts as per the optimized conditions in the hydrodynamic cavitation reactor. The results of this conventional batch experiment in terms of the rate of reaction and the conversion were compared with the results of hydrodynamic cavitation reactor system as shown in Fig. 4. It was observed that higher conversion was obtained for hydrodynamic cavitation reactor (93.5% in 30 min) as compared to the Stirred tank reactor (88.5% in 45 min) for the similar reaction conditions such as 4.5:1 molar ratio, 0.55 wt% KOH and 45 °C temperature. Similarly, the rate of reaction for hydrodynamic cavitation reactor was very high and only 20 min are required to get the maximum conversion while the stirred tank reactor took almost 1 h to reach for the maximum conversion. Earlier reports also show the longer reaction time where waste frying oil is catalyzed using cheaper CaO catalyst [23,24]. Since hydrodynamic cavitation
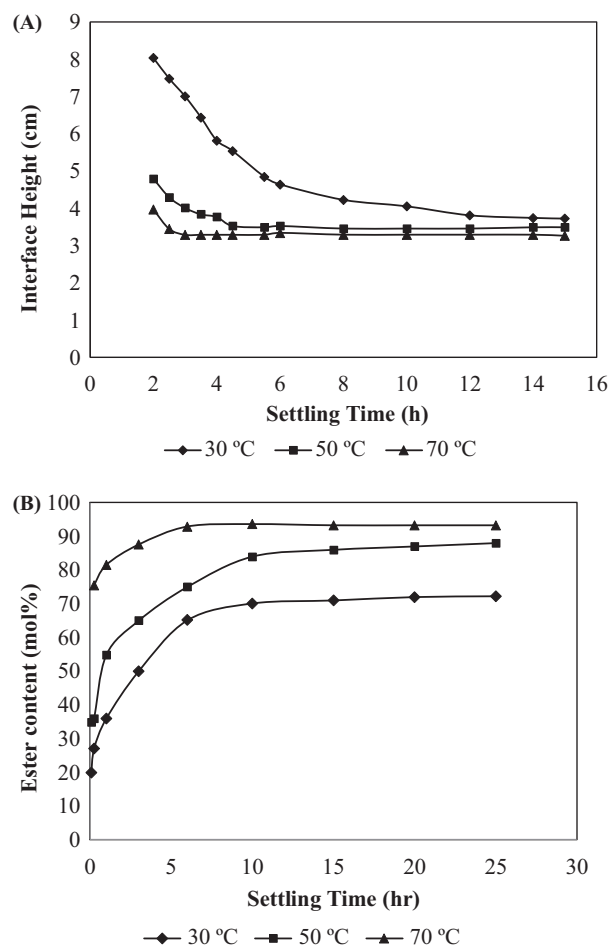
(A)

(B)
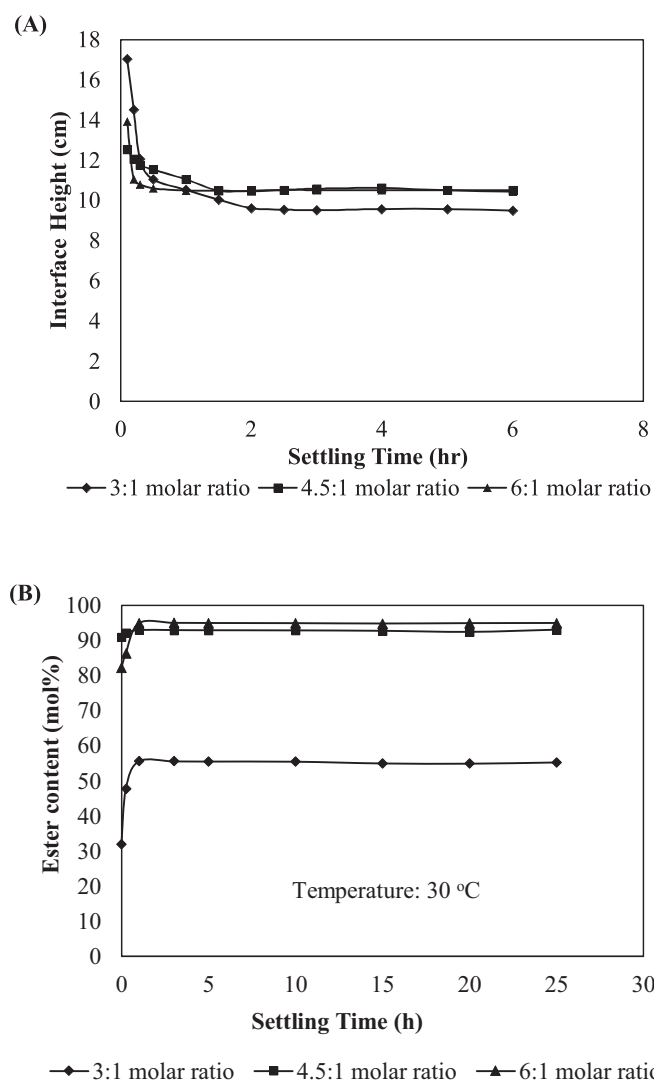
Fig. 5. (A) Effect of methanol to oil molar ratio on separation rate of methyl ester and glycerol layer (Interface Height vs. Time). (B) effect of methanol to oil molar ratio on separation rate of methyl ester and glycerol layer (Ester content vs. Time).

(A)

(B)

Fig. 6. (A) Effect of temperature on separation rate of methyl ester and water layer in washing step (Liquid interface height vs. Time). (B) effect of temperature on separation rate of methyl ester and water layer in washing step (Ester content vs. Time).

has an enhancement effect on the transesterification reaction in terms of mixing immiscible liquids due to emulsification, better results in terms of reaction rate as well as conversion were obtained. It also results in less requirement of molar ratio of methanol to oil as well as less KOH concentration relative to classical method which will reduce the cost of purification. Thus, the hydrodynamic cavitation reactor not only increases the conversion and yield in a short period of time but also reduces the quantity of alkali (KOH) requirement, which further helps to reduce the separation time.

3.4. Separation of biodiesel

3.4.1. Effect of methanol to oil molar ratio on separation rate of methyl ester and glycerol layer

The excess methanol in reaction mixture affects the separation rate of methyl ester and glycerol layer. Hence, the separation of methyl ester and glycerol layer at different methanol to oil molar ratio was studied. Fig. 5(A) shows that the phase separation by sedimentation was started in 10 min of settling. However, the ester layer was opaque indicating that the separation was incomplete. Experimental results showed that after getting enough time

for complete settling, the opaque ester phase could turn transparent. The separation study of change in liquid interface height with time for all three methanol to oil molar ratio of 3:1, 4.5:1 and 6:1, shows that the complete separation occurred within 2 h These results were confirmed by determining the methyl ester content of organic layer at different time intervals and are consistent as shown in Fig. 5(B). Most of the investigators reported that as the methanol content of the reaction mixture increases beyond 6:1 methanol to oil molar ratio, the rate of separation of methyl esters and glycerol decreases because of the increase in solubility of glycerol and ester in methanol. But Felizardo et al. [25] observed that the increase of the methanol (in excess) facilitates the separation of the glycerol from the methyl esters phase. The result obtained in this study was also in line with the results of Felizardo et al. [25]. In sedimentation studies, the layer separation rates with 4.5:1 and 6:1 molar ratio of methanol to oil were greater than 3:1. The separation time required for reaction mixture of 4.5:1 and 6:1 molar ratio was 1 h while it was 2 h for the reaction mixtures of molar ratio of 3:1. From these results it can be concluded that in cases of 4.5:1 and 6:1 methanol to oil molar ratio, due to complete transesterification reaction, the intermediate diglycerides and monoglycerides present in the reaction mixture were less which has greater miscibility in methanol as well as glycerol. This causes the complete separation of methyl ester and glycerol layer without hindrance in a very short time period of 1 h.

3.4.2. Effect of temperature on separation rate of methyl ester and water layer in washing step

Fig. 6(A) and (B) show the effect of temperature on separation rate as well as degree of separation of methyl ester and water in washing step at three different temperatures of 30 °C, 50 °C and 70 °C. The emulsion was formed when the water was mixed with the methyl ester layer (separated from glycerol) because of the presence of soap which reduced the rate of separation of ester and water. However, the lower amount of KOH, soap present in ester layer reduces the stability of emulsion formed during water washing step and further helps for faster layer separation. Similarly, intermediates diglycerides and monoglycerides which act as emulsifying agent are also present in very small amount which is additional benefit. In addition, at higher temperatures the breaking of emulsion took place and also the viscosity of the ester reduced than that at ambient temperature. Thus, the separation rate of washing step was increased at 50 and 70 °C and the significant influence of temperature on the separation rate was observed. At the temperatures of 30 °C, 50 °C and 70 °C, the complete separation was achieved at 15, 5 and 3 h respectively. At higher temperatures, the viscosity of the ester layer decreases and the separation takes place fast.

After separation, the properties of the esters were tested and found in the range of the standard specifications. The acid value of esters after the purification step was 0.47 mg KOH/g oil. The density of the biodiesel obtained after washing was 0.895 g/cm^3 and the flash point obtained was 188 °C.

4. Conclusions

The study of biodiesel production using hydrodynamic cavitation as well as separation and purification study of methyl esters yielded encouraging results.

- The maximum conversion of 93.86 mol% and product yield 93.5 wt% was achieved under the process conditions i.e. methanol to oil molar ratio of 4.5:1 and catalyst (KOH) concentration of 0.55 wt % on oil basis.
- Hydrodynamic cavitation is a potential technology that can be used for biodiesel production from used frying oil at industrial scale due to its easy scale-up property.
- Due to reaction completion, less quantity of intermediates-monoglycerides and diglycerides was presents in the ester layer that results faster separation (2 h) of the layers.
- A positive influence of high temperature on the separation rate of methyl ester and water layer in washing step was observed.
- At 30 °C, 50 °C and 70 °C temperatures the complete separations were observed in 15, 5 and 3 h respectively.

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