

Ultrasound-Assisted Synthesis of Biodiesel from Palm Fatty Acid Distillate

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The present work aims at exploiting palm fatty acid distillate as a starting raw material for synthesis of biodiesel with the aim of reducing the cost of production. Esterification of palm fatty acid distillate (PFAD) with methanol in the presence of concentrated H_2SO_4 as a catalyst has been investigated in the presence of ultrasonic irradiations at 22 kHz frequency and 120 W as supplied power dissipation. The effect of different operating parameters such as molar ratio of reactants, catalyst quantity, and operating temperature have been studied with the aim of process optimization. It has been observed that ultrasound significantly enhances the rate of reaction and also the extent of equilibrium conversion. A certain degree of conversion attributed to heterogeneity of the system, which adds to mass transfer resistances under conventional approach, appears to get eliminated due to ultrasound. Conversion levels of more than 90% have been observed with the use of ultrasound in about 150 min under ambient operating conditions.

1. Introduction

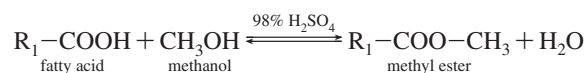
Use of biodiesel has become attractive in recent years because of its environmental benefits as compared to fossil fuels and also due to the fact that there are limited fossil fuel reserves globally, which will exhaust in the coming years due to ever increasing demand for the same. Biodiesel also has many advantages over petroleum diesel fuel, such as producing less smoke, particulate emissions, and lower carbon monoxide; having higher cetane number; and being biodegradable and nontoxic. Biodiesel also has a relatively high flash point (150 °C), which makes it less volatile and safer to transport or handle than petroleum diesel.¹ In brief, these merits of biodiesel make it a good alternative to petroleum-based fuel and have led to its use in many countries, especially in environmentally sensitive areas. The cost of synthesis of biodiesel, however, is the main hurdle for the commercialization of the product. However, due to ever increasing crude oil prices, limited resources of fossil oil, and environmental concerns, there has been a renewed focus on the ways to minimize the cost of biodiesel production. The problem can be approached in two different ways: by finding a cheap source of raw material^{2–4} or by intensifying the synthesis process by using novel reactors based on the use of enzymes, microwaves, supercritical fluids, ultrasound, or fluid energy.^{5–9}

The most popular method of producing biodiesel is the transesterification of vegetable oils.^{5,6} Biodiesel obtained by the transesterification process can be a mixture of monoalkyl esters of higher fatty acids. The substantially higher costs of vegetable oil makes pure vegetable oil an unfavorable starting raw material. However, if waste cooking oil or a mixture of off-specification oil or fatty acid cuts is used in a conventional approach of synthesis, significantly lower rates of reaction are observed with the requirement of severe operating conditions. The conventional techniques based on use of stirring typically utilize temperatures in the range of 70–200 °C, pressures in the range of 6–10 atm, and reaction times of up to 70 h for achieving conversions in the range of 90–95 mol % based on the type of raw material used, the type and concentration of the catalyst, and the percentage excess of alcohol.^{10–12} The lower rates of synthesis have been typically attributed to mass transfer limitations due to heterogeneous conditions existing during the

reaction. Use of cavitation reactors can favor the reaction chemistry and propagation by way of enhanced mass transfer and interphase mixing between the phases and also can lower the requirement of the severity of the operating conditions in terms of temperature and pressure.¹³ Indeed, there have been some earlier illustrations referring to the use of cavitation reactors for intensification of biodiesel synthesis^{5,7,14–16} but mainly these have been based on the use of pure vegetable oils as a raw material for the synthesis. A recent study⁴ by our group reported the use of a fatty acid cut as an alternative, cheaper starting material. In continuation of our objective of utilizing cheaper raw materials for the synthesis of biodiesel using cavitation reactors, the present work reports the use of palm fatty acid distillate (PFAD), which is generated as a byproduct during the refining of palm oil and has a comparatively much lower value as compared to the palm oil. The esterification reaction between PFAD and methanol in the presence of sulfuric acid as a catalyst and ultrasonic irradiations as a source for generation of cavitation conditions has been carried out.

2. Materials and Methods

2.1. Reaction Scheme. The reaction considered for the present study is a typical esterification reaction of oil and alcohol in the presence of acid catalyst producing methyl esters and water. The reaction can be schematically represented as



This reaction is a typical reversible endothermic reaction. To shift the equilibrium of the reaction toward the desired methyl esters, usually methanol has to be taken in excess and an operating ratio as high as 1:70 (oil to methanol ratio) has been reported.¹⁷ Use of ultrasound or in general cavitation reactors, however, also helps in significantly reducing this excess requirement of alcohol.^{4,15}

2.2. Materials. Palm fatty acid distillate was obtained from Godrej Ind. Ltd. (Mumbai, India). It had the different components as palmitic acid (46.81%), oleic acid (35.31%), stearic acid (4.72%), linoleic acid (8.38%), and others (4.76%). Methanol and sodium hydroxide were procured from SD Fine-Chem Pvt. Ltd. (Mumbai, India). Sulphuric acid (98%) was procured from Merck Ltd. (Mumbai, India).

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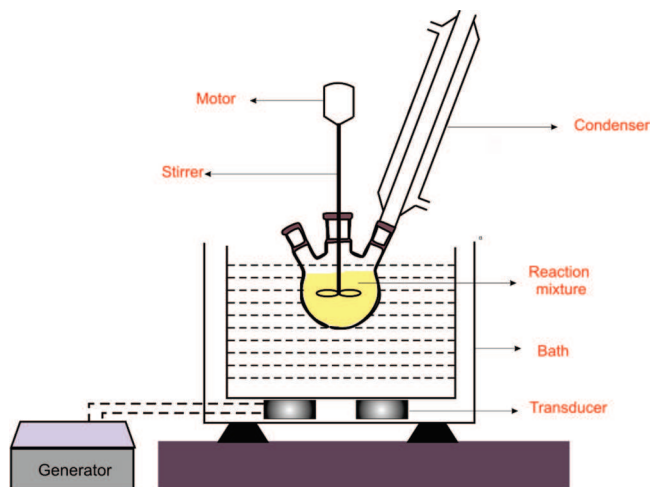


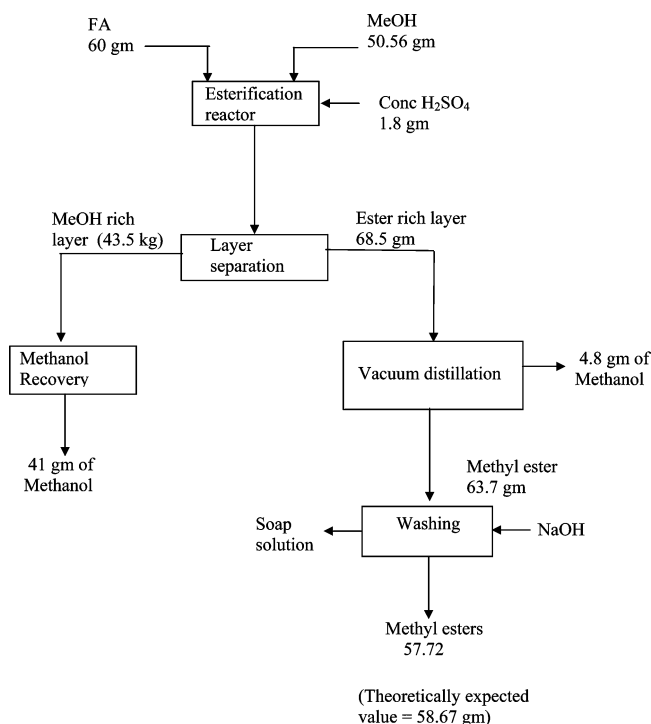
Figure 1. Schematic representation of the experimental setup.

2.3. Experimental Setup. An ultrasonic bath procured from Supersonics, USA (power rating of 120 W and frequency of irradiation of 22 kHz) was used as the source of ultrasonic irradiation. The observed calorimetric efficiency for the bath¹⁸ was 36%, indicating that the actual power available for cavitation events was 43.2 W. The reactions were carried out in a three neck round-bottom flask of 250 mL capacity. A condenser was mounted on it to reflux the evaporating methanol. Initially the system is homogeneous, but it attains heterogeneity during the progress of the reaction; hence, an overhead stirrer was used whose speed could be controlled in the later stages of the reaction. The flask was arranged in such a manner that it is equidistant from all the sides of the walls such that it is exposed to maximum cavitation intensity as observed in the earlier mapping work.¹⁹ A schematic representation of the complete experimental assembly is given in Figure 1.

2.4. Experimental Procedure. Initially a known quantity of PFAD was taken and melted in the presence of agitating conditions separately. The molten PFAD was then charged to the reactor containing a measured quantity of methanol with constant stirring. A sample was taken out to determine the initial acid value. A known quantity of 98% sulfuric acid, based on the desired catalyst concentration (as a function of fatty acid quantity), was added to the reaction mixture. Sonication of reaction mixture was started with constant stirring, and samples were taken out at certain time intervals for analysis of the progress of reaction. The reaction mixture samples were titrated with 0.1 N NaOH solution to determine the amount of unconverted PFAD in terms of the acid value of the mixture. The reaction was carried out till the attainment of equilibrium conditions.

2.5. Product Separation. Usually at the end of reaction and attainment of equilibrium conversions, two distinct layers were obtained, which can be easily separated on the basis of the density difference. The upper layer consists of product and unreacted PFAD, whereas the lower layer was a combination of methanol and water of reaction along with the catalyst H₂SO₄. To separate the upper layer containing the desired product and unreacted PFAD, washing with 0.5 N NaOH solutions was done. It should be noted here that the concentration of NaOH is a critical operating parameter, as with higher concentrations of NaOH a very thick soap can be obtained. The lower layer containing methanol and water can be separated for methanol recovery by a simple distillation process due to a large difference in the boiling points. Chart 1 shows the flow diagram for a sample experimental run. The extent of methanol recovery and

Chart 1. Flow Diagram with Material Balance



Recovery of methanol = 90.58 %

Recovery of Methyl esters = 98.39 %

product yield were always greater than 95% for all the investigations carried out in this work.

3. Results and Discussion

During the study of this esterification reaction, the effects of various parameters such as the presence of ultrasound, molar ratio of reactants, catalyst concentration, and reaction temperature on the rate of reaction as well as equilibrium conversion have been investigated. We now discuss the obtained results in the following sections.

3.1. Effect of Ultrasound. The effect of ultrasound on the rate of reaction and equilibrium conversion was investigated at two different operating temperatures of 30 and 40 °C and at constant reactant molar ratio (1:7) and catalyst concentration (3% of PFAD). The obtained results of these sets of reactions are depicted in Figure 2. It can be clearly seen from the figure that initially there is not much effect on the rate of reaction, possibly attributed to the homogeneous conditions of the reaction mixture and the reaction between PFAD and alcohol being very fast. Beyond a critical extent of conversion of about 30%, ultrasound has significant effects on the progress of reaction. At this stage, the system becomes heterogeneous as observed visually and the overall progress of the reaction is governed by the mass transfer between the phases. The liquid circulation currents generated by the stirrer, which help in uniform mixing at the macrolevel, are not sufficient to eliminate the mass transfer limitations, resulting in lower rates of reactions. On the other hand, ultrasound-generated cavitation results in conditions of intense turbulence at the microscale and uniform mixing of the two phases at the microlevel and hence in elimination of the mass transfer resistances.²⁰ The observed trends were similar at both the operating temperatures. To give a quantitative idea about the observed intensification due to the use of ultrasound, conversion of about 95% was achieved in 150 min at 40 °C, whereas only stirring required about 300 min for yielding a

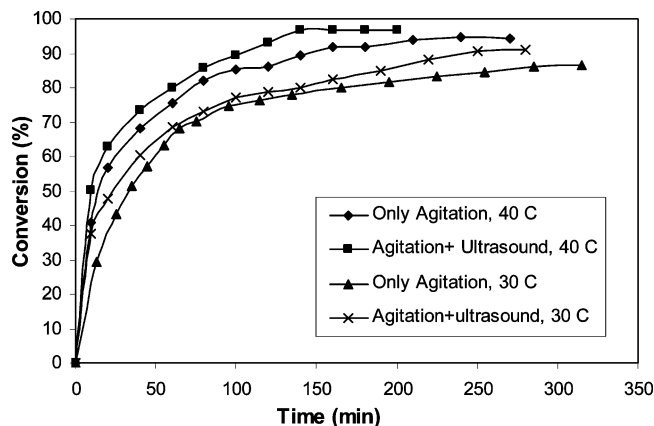


Figure 2. Effect of presence of ultrasound on the rate of reaction and equilibrium conversion.

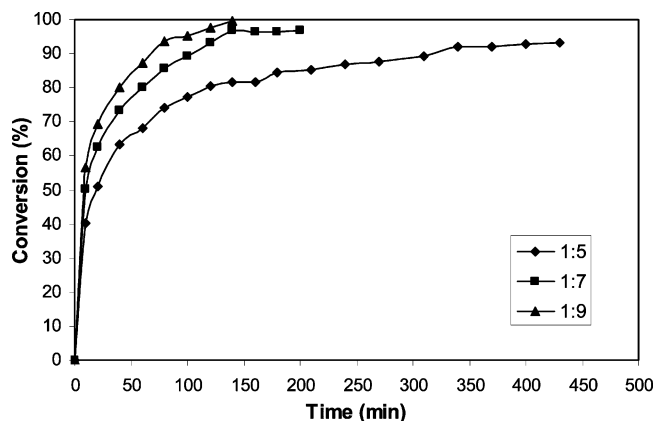


Figure 3. Effect of molar ratio on the rate of reaction and equilibrium conversion.

conversion of around 93%. Credence to the proposed role of ultrasound in enhancing the mass transfer between the species and hence increasing the overall rates of reaction can be obtained from an earlier investigation by Wen et al.²¹ on esterification of palmitic acid at different levels of power dissipation. Wen et al.²¹ reported that the yield of the reaction was directly dependent on the supplied power; it was around 60% at no ultrasonic power and linearly increased to more than 90% at maximum supplied power. It is expected that, with an increase in the power dissipation, the intensity of turbulence as well as liquid circulation currents increases.²²

3.2. Effect of Molar Ratio. The esterification reaction between PFAD and methanol follows a reversible path. Higher equilibrium conversion can only be obtained if the backward reaction is minimized. There are two ways to reduce the rate of backward reaction: (a) to remove one of the undesired products, i.e. water in the present case, continuously or (b) to use one of the reactants in excess (alcohol in this case). In the present system, it is not easy to remove water, as the boiling point of methanol (64.7 °C) is much lower than the boiling point of water (100 °C). Thus, the option of using excess methanol has been employed in the present study. The reaction has been carried out with 1:5, 1:7, and 1:9 molar ratios of PFAD to methanol while the reaction temperature was kept constant at 40 °C and the catalyst concentration was kept constant at 3 wt % of PFAD. The obtained results are depicted in Figure 3. As observed, the equilibrium conversion increases with an increase in the methanol-to-fatty acid mole ratio under otherwise identical conditions. The equilibrium conversion of PFAD increased from about 93% at a feed mole ratio (acid to alcohol) of 1:5 to about

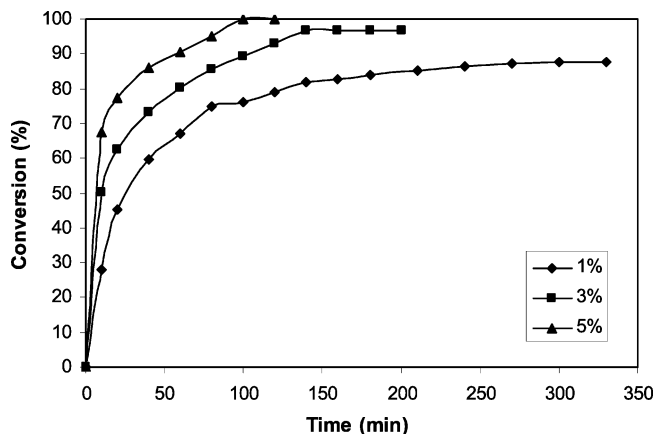


Figure 4. Effect of catalyst concentration on the rate of reaction and equilibrium conversion.

100% at a feed mole ratio (acid to alcohol) of 1:9. It can also be observed that there is a significant increase in the rate of reaction: with 1:5 mole ratio, it took about 430 min to reach equilibrium conversion of 93%, whereas with 1:9 mole ratio, the equilibrium conversion was achieved in only 140 min. With an increase in the feed molar ratio, the quantity of methanol in the reaction mixture increases, which mainly affects the cavitation intensity. Excess methanol provides additional cavitation events in the reactor, leading to formation of enhanced emulsion quality (smaller drop sizes), providing additional area for the reaction and hence increased conversion. Stavarache et al.¹⁵ have reported similar effects of the use of excess methanol leading to an enhanced number of cavitation events and hence enhanced conversion of vegetable oil in transesterification. Excess methanol also favors the removal of water of reaction as aqueous phase, thereby not hindering in the progress of reaction.⁵ It can be also seen from the figure that the extent of increase in the equilibrium conversion and rate of reaction is much more for an increase in the mole ratio from 1:5 to 1:7 as compared to that observed for an increase in the mole ratio from 1:7 to 1:9. It should be also noted here that using additional methanol, although speeding up the reaction, also increases the separation (methanol recovery) load on the system (only a specific amount of methanol is required for the actual reaction and hence any excess would contribute to the separation load); hence, an optimum operating ratio should be selected on the basis of overall economics and the equilibrium conversion. Over the range of the molar ratios investigated in the present work, the 1:7 molar ratio appears to be the optimum molar ratio.

3.3. Effect of Catalyst Concentration. To study the effect of catalyst concentration on the rate of reaction and equilibrium conversion, the reaction was carried out at three different catalyst loadings of 1%, 3%, and 5% of the amount of PFAD used. The reaction temperature was kept constant at 40 °C and molar ratio of PFAD to methanol was 1:7 for all reactions. The results are shown in Figure 4. One can observe that there is a significant increase in the rate of reaction as well as the equilibrium conversion attained by the system as the catalyst loading increases from 1% to 5% under otherwise identical conditions. The results obtained are quite expected as per classical catalysis effects and also are similar to those reported for the ultrasound-assisted synthesis processes.^{21,23} The main role of sulfuric acid is to make protons available in the palm fatty acid phase in sufficient quantity (due to partitioning) to catalyze the reaction at a reasonable rate. The water formed during the esterification reaction dilutes the sulfuric acid, which in turn reduces the availability of protons in the palm fatty acid phase, slowing the

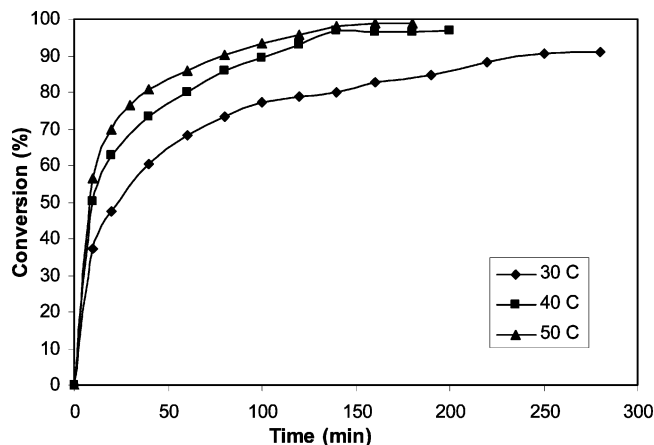


Figure 5. Effect of reaction temperature on the rate of reaction and equilibrium conversion.

reaction. Using a higher concentration of sulfuric acid partly nullifies the dilution effect, and hence, the overall rate of reaction increases with an increase in the concentration of sulfuric acid. Higher sulfuric acid concentration in alcohol, due to its higher density, also assists in the easy separation of phases after completion of the reaction.

3.4. Effect of Reaction Temperature. The effect of temperature on the rate of reaction and equilibrium conversion was also studied by carrying out the reaction at three different temperatures of 30, 40, and 50 °C. The molar ratio of PFAD to methanol was kept constant at 1:7 and the catalyst concentration was kept at 3% by weight of PFAD used. The results for the reactions at different temperatures are given in Figure 5.

It has been observed that there is only a slight increase in the rate of reaction up to a certain critical level of conversion (50–60% in the present case), as the initial reaction is very fast. Beyond this critical level, there is a significant increase in the rate of reaction as well as the equilibrium conversion attained by the system. This might be due to the fact that esterification is an endothermic reaction as well as the system attains heterogeneity, separating out into two layers at the later stage of reaction, one a methanol-rich phase and the other an ester-rich phase at lower temperature. The reaction occurs in the ester layer, where there is much less methanol due to its low solubility in the ester layer, resulting in the overall lower rates of reaction. With an increase in the temperature, there is an increase in the solubility of methanol in the ester phase, resulting in a corresponding increase in the rate of reaction. Also, with an increase in the temperature, the solubility of water formed during the reaction in methanol increases, overcoming the equilibrium limitations. It is clear from the graph that the increase in the rate of reaction and equilibrium conversion for the temperature change from 30 to 40 °C is considerably high as compared to the observed increase when the temperature change was from 40 to 50 °C. Grooten et al.²⁴ have reported similar effects of temperature in ultrasound-assisted esterification reactions.

3.5. Kinetic Modeling. An attempt was made to develop a kinetic model for the esterification reaction, as there is absolutely no information on the kinetic data for ultrasound-assisted synthesis of biodiesel. It has been observed from the profiles of the conversion against time of reaction that the reaction follows a two-stage path. In the initial period, the reaction rate is significantly higher, and beyond a critical concentration, the rate of reaction lowers down. Initially, the system is completely homogeneous due to the presence of excess methanol and the reaction is mainly dependent on the concentration of fatty acid.

However, after certain conversion, the system attains heterogeneity (separation of layers occurs). In the first stage, as methanol is used in excess of fatty acid, the reaction follows a typical first-order behavior with respect to fatty acid. In second stage of reaction, heterogeneity is attained, the methanol phase separating from a layer consisting of ester and fatty acid. As methanol has very low solubility (maximum of about 8% at 30 °C) in the ester-rich phase where the reaction is taking place, the reaction depends on the concentration of methanol in addition to the concentration of fatty acid. It can be also assumed that in the presence of ultrasonic irradiations, the concentration of methanol in the ester-rich phase is constant, due to the maximum supply of methanol in this phase because of enhanced interphase mixing. It is assumed that, as the dissolved methanol gets consumed for the reaction, the excess methanol present in the form of a separate layer releases methanol (by the process of mass transfer facilitated by cavitation) in to the ester layer, maintaining the 8% solubility level. The credence to this hypothesis can be obtained from earlier results of enhanced rates of reaction in the presence of ultrasound only beyond the critical conversion levels. Thus, the overall reaction can be considered to be second-order with respect to fatty acid in the later stages.

For the first stage, with excess of methanol, the rate equation can be represented as

$$-r = \left(\frac{-d(\text{FA})}{dt} \right) = k_1 \times \text{FA}$$

where FA = the concentration of fatty acids (g/mL) and k_1 = the rate constant for a first-order reaction (s^{-1}).

For the second stage, at a lower concentration of fatty acid and since the methanol concentration is assumed to be constant, the reaction has been modeled as second-order with respect to fatty acid. The rate equation for this second stage can be represented as follows

$$(-r) = \left(\frac{-d(\text{FA})}{dt} \right) = k_2 \times (\text{FA})^2$$

where k_2 = the rate constant for second order reaction ($\text{mL}^1 \text{g}^{-1} \text{s}^{-1}$).

Now by combining the rate equations for these two stages, the proposed rate equation for the complete process is given by

$$-r = \left(\frac{-d(\text{FA})}{dt} \right) = \frac{k_1 \times \text{FA}^2}{(1 + k_2 \times \text{FA})}$$

In terms of conversion,

$$\frac{dX}{dt} = \frac{k_1 \times \text{FA}_0 \times (1 - X)^2}{[1 + k_2 \times \text{FA}_0 \times (1 - X)]}$$

where X = the fractional conversion of fatty acid.

The kinetic parameters of this reaction under different conditions have been estimated by using Matlab solver. A trial and error method was used to get the kinetic parameters, in which initially some values were assumed for the rate constants (k_1 and k_2) and the rate equation was solved by using these values to estimate conversion against time data. The obtained data were then compared with the experimental data, and the rate constant values were changed accordingly to get a reasonably good fit. The optimized values of kinetic parameters are given in Tables 1–3 for different reaction conditions. The explanation for variation in the obtained values with the reaction conditions has already been offered in the earlier sections. It should be noted here that the generated model in the present work is only a starting point in this needed field of kinetic data

Table 1. Kinetic Parameters for Reactions at Different Operating Temperature

no.	temperature (°C)	k_1 s ⁻¹	k_2 (mL g ⁻¹ s ⁻¹)
1	30	0.001 59	0.0126
2	40	0.008 17	0.1076
3	50	0.014 01	0.1726

Table 2. Kinetic Parameters for Reactions at Different Mole Ratios of Reactants

no.	molar ratio (PFAD/MeOH)	k_1 s ⁻¹	k_2 (mL g ⁻¹ s ⁻¹)
1	1:5	0.001 42	0.0126
2	1:7	0.008 17	0.1076
3	1:9	0.032 51	0.5059

Table 3. Kinetic Parameters for Reactions at Different Concentrations of Catalyst

no.	catalyst concn (% of PFAD)	k_1 s ⁻¹	k_2 (mL g ⁻¹ s ⁻¹)
1	1	0.001 02	0.0017
2	3	0.008 17	0.1076
3	5	0.041 42	0.5792

for ultrasound-assisted esterification reactions, which is lacking in the literature.

4. Conclusions

Cavitation generated using ultrasonic irradiation can be effectively used for synthesis of biodiesel from palm fatty acid distillate, a comparatively much cheaper raw material, as compared to vegetable oils. Cavitation mainly affects the mass transfer rates and ensures uniform distribution of the reactants, as concluded from the fact that significant effect on the rate of reaction and equilibrium conversion is only observed in later stages of the reaction when heterogeneity sets in. The optimum operating parameters for the present work were observed to be 1:7 mole ratio of PFAD to methanol, 5% catalyst concentration, and 40 °C. A kinetic model based on a two-stage progress for the overall reaction was developed and the obtained values of the rate constants suitably explained the variation of the operating parameters. The recovery of methanol as well as final product was always more than 90%. The present work has clearly demonstrated the key role of cavitation reactors in the process intensification of biodiesel synthesis process.

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Received for review June 24, 2008

Revised manuscript received October 6, 2008

Accepted October 16, 2008

IE800981V