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Ultrasound assisted transesterification of waste cooking oil using heterogeneous solid catalyst

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ABSTRACT

Transesterification based biodiesel production from waste cooking oil in the presence of heterogeneous solid catalyst has been investigated in the present work. The effect of different operating parameters such as type of catalyst, catalyst concentration, oil to methanol molar ratio and the reaction temperature on the progress of the reaction was studied. Some studies related to catalyst reusability have also been performed. The important physicochemical properties of the synthesized biodiesel have also been investigated. The results showed that tri-potassium phosphate exhibits high catalytic activity for the transesterification of waste cooking oil. Under the optimal conditions, viz. catalyst concentration of 3 wt% K_3PO_4, oil to methanol molar ratio of 1:6 and temperature of 50 °C, 92.0% of biodiesel yield was obtained in 90 min of reaction time. Higher yield was obtained in the presence of ultrasound as compared to conventional approach under otherwise similar conditions, which can be attributed to the cavitational effects. Kinetic studies have been carried out to determine the rate constant at different operating temperatures. It was observed that the kinetic rate constant increased with an increase in the temperature and the activation energy was found to be 64.241 kJ/mol.

1. Introduction

Significant variation in the global prices of petroleum crude oil has an adverse impact on the national economy of crude oil dependant countries and developing countries such as India. The petroleum crude oil consumption in India was 148 million metric tonne per year in 2011–12 and demand for petroleum products was 141.79 million metric tonne. Diesel constitutes almost about 35.5% of all the petroleum product consumption in India. According to data from the Ministry of Petroleum and Natural gas, 8.2% of the total diesel consumed is for power generation where as agricultural activities use about 12.2% and transport guzzles a maximum of 65.3%. Apart from reducing the dependency of economy on the fossil fuels, depletion of petroleum sources and environmental concerns have also induced a recent interest in finding alternative sources for petroleum based diesel fuels [1].

Transesterified oil which is also commonly known as biodiesel can be a good alternative to petroleum based diesel. By chemical structure, biodiesel is mono-alkyl ester of long chain fatty acid that can be synthesized from a renewable lipid feedstock like used vegetable oil or animal fats. Generally biodiesel is considered as an oxygenated, renewable, biodegradable, environment friendly fuel with similar physical properties as that of petro-diesel with comparatively low emission profile [2]. Biodiesel can be produced using transesterification reaction between oil and alcohol in the presence of homogeneous or heterogeneous or enzymatic catalyst with glycerol as a by-product as shown in Scheme 1. Many alcohols can be used in transesterification reaction such as methanol, ethanol and isopropyl alcohol etc. but the most commonly used alcohol is methanol due its low cost and easy availability. Biodiesel production has a major problem in commercialisation in that the cost of biodiesel produced is about 1.5 times more as compared to that of petroleum based diesel. The production of biodiesel is economically not viable because of cost of raw materials, energy requirements for production and separation costs for the generally used homogeneous catalyst [3–4]. The present study reports an approach based on the use of waste cooking oil as a low cost feed stock and also the use of heterogeneous catalyst to minimise ease of separation. The studies related to the ultrasound induced intensification of biodiesel synthesis based on the use of heterogeneous catalyst and waste cooking oil are scarce and hence the present work is important.

Patil et al. [5] reported that about 4.1 kg of Waste Cooking Oil (WCO) is produced per person in a year. Considering the present

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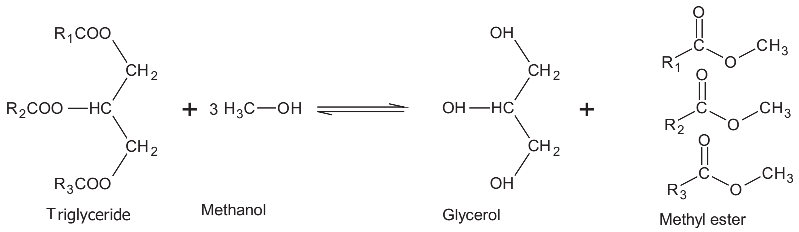

Scheme 1. Transesterification reaction of triglyceride with methanol.

scenario of world population as nearly 7.18 billion, around 29 million tons of WCO will be produced in a year. Disposal of WCO is a major task due to dumping problems and possible pollution of the land resources and water [6]. All these facts indicate that used cooking oil should be recycled and one of the options can be use as a potential source for biodiesel production. Heterogeneous catalyst has advantages like being non-corrosive, environmentally benign and present fewer disposal problems [7]. Also they are much easier to separate from liquid products and can be possibly reused [8]. Many researchers have reported the use of various heterogeneous catalysts like oxides, mixed oxides, phosphates, sulphates etc. [9]. The possible process intensification mechanism for synthesis of biodiesel using ultrasound is that ultrasound helps in the formation of fine emulsion of two immiscible liquids, generating large interfacial area and due to this fact transesterification reaction of waste cooking oil and methanol can reach equilibrium in a shorter time with a high yield of alkyl esters even at lower operating temperature. The enhancement in the mass transfer and interphase mixing between the heterogeneous reactant phases is also helpful in giving enhanced yields [10].

In the present work, potassium and sodium phosphate have been used as the heterogeneous catalysts for transesterification of waste cooking oil. Since phosphates of potassium and sodium are insoluble in methanol, such a process possesses the advantage of easy recovery of the used catalyst from the reaction medium. The influence of various reaction parameters, such as type of catalyst and its loading, oil to methanol molar ratio (OMMR), reaction temperature and catalyst reusability on the yield of fatty acid methyl ester (FAME) has been investigated. Kinetic constant as well as activation energy for the transesterification reaction have been also determined at optimum operating conditions. Also, the properties of the synthesized biodiesel have been evaluated in order to compare with ASTM standards.

2. Materials and methods

2.1. Materials

Waste cooking oil was obtained from a local restaurant in Mumbai. The procured WCO was subjected to 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. Table 1 gives the properties of treated WCO being used as feed stock for biodiesel production. As the free fatty acid content in the WCO obtained was observed to be very less (less than 2% i.e. acid value of 3.75), WCO was used directly for the transesterification reaction without any deacidification treatment. Methanol (99%) (AR grade), different catalysts viz. K_3PO_4, Na_3PO_4, Na_2HPO_4, NaH_2PO_4, KH_2PO_4 and molecular sieves were procured from M/s S. D. Fine Chem. Ltd., Mumbai. All the catalysts used in the present work were in powder form. Acetonitrile and acetone (HPLC grade) used as solvent for HPLC analysis were procured from M/s Hi Media, Mumbai whereas methyl oleate and methyl linoleate standards were procured from Sigma–Aldrich.

Table 1
Physical and chemical properties of waste cooking oil.

Property	Value
Physical	
Saponification value (mg KOH/g of oil)	207.7
Density (kg/m^3)	928
Acid value (mg KOH/g oil)	3.75
Viscosity (mm^2/s)	96.55
Water content (%)	0.7
Fatty acid composition	
Linoleic acid (%)	73.4
Oleic acid (%)	18.3
Palmitic acid (%)	6.7
Stearic acid (%)	1.6

2.2. Experimental methodology

The transesterification experiments were performed in a 200-mL three-neck batch reactor with a diameter of 55 mm. The three openings in the reactor were used for accommodating the condenser (to condense the evaporating methanol), introduction of ultrasonic horn having diameter of 12 mm or stirrer (based on the approach of ultrasound assisted or the conventional approach) and 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 used vegetable oil and heterogeneous catalyst and heated to the desired reaction temperature. Once the desired temperature was achieved, known quantity of methanol was added to the reactor. The biodiesel yield was determined by sampling 3 ml of the mixture at different pre-designated time. The withdrawn samples were centrifuged, and the upper phase was withdrawn and the samples were washed with water in order to remove the excess methanol from the mixture. Finally, molecular sieves (3 Å) were added to each sample to adsorb the trace amount of moisture. Samples were then finally analysed using HPLC as per the details described later. The different operating parameters used in the present work to optimise the yield of biodiesel from waste cooking oil, include type of heterogeneous catalysts (K_3PO_4, Na_3PO_4, Na_2HPO_4, NaH_2PO_4 and KH_2PO_4), catalyst concentrations (1, 2, 3 and 4% by weight of the charged oil), oil to methanol molar ratios (1:4, 1:6 and 1:8) and operating temperatures (30, 40, 50 and 60 °C) at fixed 50% amplitude (supplied power of 375 W) of ultrasonic horn of frequency 22 kHz. Calorimetric study has been carried out with known amount of methanol where the time required to increase the temperature by 15 °C was measured. The energy transfer efficiency at different percentage amplitude from 30 to 90% has been calculated based on the input energy (percentage amplitude × rated power) and actual energy dissipation ($m \times Cp \times \Delta T$) into the methanol solution. From Fig. 2, it can be established that maximum energy

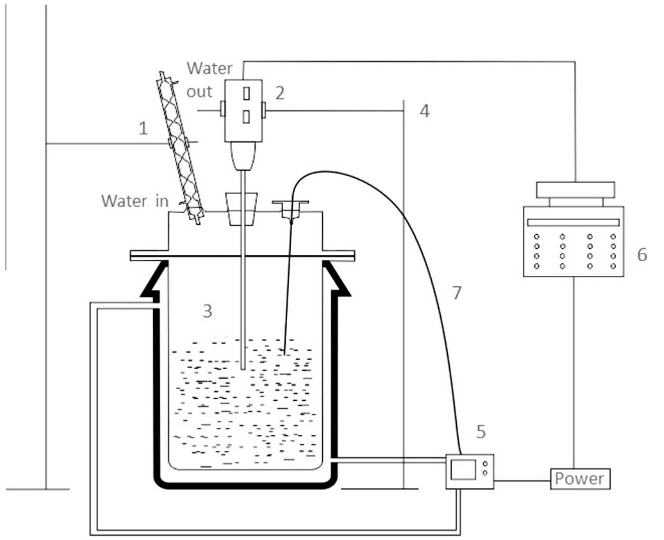

Fig. 1. Schematic representation of experimental setup. (1) Condenser, (2) Ultrasonic horn, (3) Reactor (200 ml), (4) Stand support, (5) Temperature controller bath, (6) Ultrasonic generator, (7) Temperature sensor.

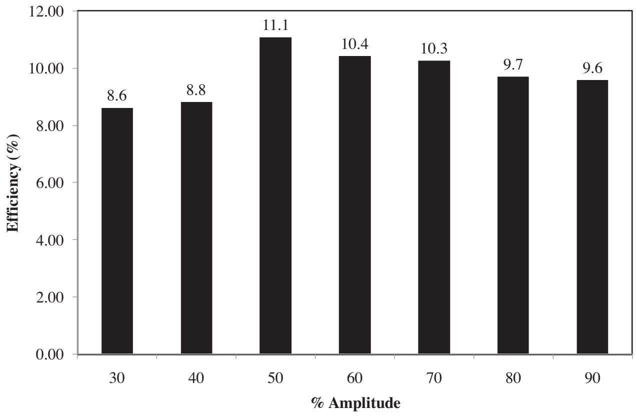

Fig. 2. Calorimetric study for finding the energy efficiency at different amplitudes.

transfer efficiency of ultrasonic horn is obtained at percentage amplitude equal to 50%, and hence transesterification experiments were carried out at ultrasound horn amplitude of 50% (supplied power of 375 W).

Experiments were also performed using conventional approach based on the use of overhead stirrer under optimised 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 pitched blade turbine impeller having six blades with a diameter of 1.5 cm was used as the stirrer and the operating speed used in the work was 1000 rpm. At this speed of rotation, it is expected that mixing at macro scale would be uniform and hence there will not be any mass transfer limitations. 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.

2.3. Analysis

The acid value and saponification value of waste cooking oil were determined using standard titration method [16]. Molecular weight was determined from saponification and acid value. Water present in oil was determined using a Karl-Fischer titrator (MKC-610, Kyoto Electronic Manufacturing Co. Ltd.,). The fatty acid composition of triacylglycerols was determined by converting all fatty acids of triacylglycerols 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 analysed using HPLC analysis (Agilent Eclipse XDB C-18, 5 μm, length 4.6 × 250 mm column using RI detector). The samples were analysed isocratically using mobile phase of acetonitrile: acetone (70:30) with 1.5 ml/min flow rate. Samples were prepared using 10 μl of the reaction mixture diluted with 10 ml of mobile phase. A typical HPLC chromatogram is represented in Fig. 3. The concentration was calculated based on the area under the peak obtained for the retention time of standard samples of methyl oleate and methyl linoleate.

2.4. Kinetic rate constant

The transesterification reaction consists of three mole-equivalents of the alcohol (methanol in this case) reacting with a triglyceride (TG), in a stepwise manner giving diglyceride, monoglyceride, and finally free glycerol. One mole equivalent of the corresponding ester is produced in each step of these reversible reactions [11]. Salamatiniaa et al. [12] reported kinetic analysis for the ultrasound assisted transesterification of palm oil in the presence of heterogeneous catalyst (strontium oxide) at different temperatures (55, 60 and 65 °C). It has been reported that due to the high mixing ability of ultrasound induced cavitation, the reaction mixture can be assumed as a homogenous system. The transesterification of triglyceride due to the presence of excess methanol can be considered as an irreversible pseudo second-order reaction and the rate equation may be stated as below:

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

where C_{TG} is the triglycerides molar concentration in mol/L, t is the reaction time in min, r_{TG} is the reaction rate of the triglycerides in mol/(L min) and k is the reaction rate constant in L/(mol min). By Integration Eq. (1) yields:

$$\frac{1}{C_{\mathrm{TG}}} = k \cdot t + \frac{1}{C_{\mathrm{TG}_0}} \tag{2}$$

Rearranging above Eq. (2) in terms of the conversion gives following equation:

$$\frac{X}{1-X} = C_{\mathrm{TG}_0} \cdot k \cdot t \tag{3}$$

where C_{TG_0} is molar concentration of triglyceride at time zero in mol/L and X is triglyceride conversion at any time t. Based on the information of the biodiesel yield using reaction stoichiometry, triglyceride concentration during the transesterification process can be obtained to be used in the Eq. (2). A plot of $X/(1-X)$ versus t will be a straight line if the model is valid, and k can be obtained from the slope of this line.

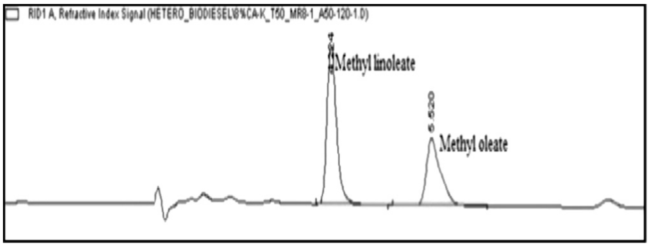

Fig. 3. HPLC chromatogram for transesterification product.

Arrhenius equation provides information about the energy of activation (Ea) based on specific reaction rate constant (k) and absolute temperature (T) which can be given as follows:

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

Where R is universal gas constant (J/(mol K)) and A is the frequency factor. The equation can be modified as:

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

A plot of $\ln(k)$ vs. $1/T$ provides slope equal to $(-Ea/R)$ and with the available information of R, activation energy can be determined.

3. Results and discussion

3.1. Effect of type of catalyst

The effect of different heterogeneous solid catalysts such as tripotassium phosphate (K_3PO_4), trisodium phosphate (Na_3PO_4), disodium phosphate (Na_2HPO_4), dipotassium phosphate (K_2HPO_4), monosodium phosphate (NaH_2PO_4), and monopotassium phosphate (KH_2PO_4) on the progress of the transesterification reaction has been investigated. Experiments were performed at molar ratio of oil to methanol as 1:6, temperature of 60 °C and catalyst concentration of 2% by weight of oil in the presence of ultrasound at 50% amplitude. The obtained results over a reaction time of 120 min have been presented in Fig. 4. It can be seen from the figure that maximum biodiesel yield of 70.5% was obtained for K_3PO_4 followed by 63.10% yield for the case of Na_3PO_4 as the catalyst. The biodiesel yield of 14.3% was obtained in the case of Na_2HPO_4, while almost no biodiesel yield was observed in the case of NaH_2PO_4, K_2HPO_4 and KH_2PO_4. The obtained results can be attributed to the fact that K_3PO_4 is relatively insoluble in methanol and oil, but readily dissolves in water. In the presence of water, K_3PO_4 and Na_3PO_4 are hydrolysed to form HPO_4^{2-} and HPO_4^{-} ions and OH^- ions in the reaction mixture. These ions give strong alkalinity to the reaction mixture which is favourable for the progress of the transesterification reaction. It was observed that higher biodiesel yield was obtained in the case of tripotassium phosphate as compared to trisodium phosphate, which is attributed to the fact that trisodium phosphate gives less alkalinity as compared to tripotassium phosphate. Also Na^+ ion gives a very stable emulsion of the product mixture resulting in difficult separation of biodiesel from glycerol and unreacted oil. Almost no conversion was obtained in the case of Na_2HPO_4, NaH_2PO_4, and KH_2PO_4 because these catalysts show low catalytic activity. Similar results have been reported by Guan et al. [13] for the transesterification of waste cooking oil with methanol using heterogeneous solid catalyst viz. tri-potassium phosphate, calcium oxide and tri-sodium phosphate. The transesterification reaction of waste cooking oil with methanol was investigated at constant temperature of 60 °C over 1 h with solid catalyst concentration of 4% (by wt) based on the oil weight and it has been reported that tri-potassium phosphate gave higher biodiesel yield as compared to calcium oxide and tri-sodium phosphate attributed to a direct correspondence with higher alkalinity. CaO is also a good catalyst for transesterification reaction, but it was found that CaO easily react with carbon dioxide in the air and gives calcium carbonate where as phosphate has no such problem. Choedkiatsakul et al. [14] also studied the application of commercial heterogeneous catalysts viz. calcium oxide (CaO) and tri-potassium phosphate (K_3PO_4) for the transesterification of refined palm oil in ultrasound-assisted and conventionally stirred reactor. It was reported that high methyl ester yields were obtained in the ultrasound assisted reactor for both CaO (90%) and K_3PO_4 (80%). Although K_3PO_4 has more basic sites than that of CaO catalyst, methyl ester yield for the K_3PO_4 catalyst was only 80%. Catalyst K_3PO_4 was used in a granular form having less surface area as compared to CaO and hence lower yield could have been obtained. Viola et al. [15] synthesized biodiesel from fried vegetable oils using tripotassium phosphate in granular form and reported that the reaction rate was mainly dependent on the active surface area of K_3PO_4. The surface area per unit volume of catalyst contributes to the catalytic effects and hence the rate of reactions. Typically lower catalyst sizes give more surface area which results into higher biodiesel yield. Viola et al. [15] carried out a transesterification reaction to produce biodiesel using K_3PO_4 in powder form and reported 93% conversion whereas Guan et al. [13] reported 72% conversion with granular K_3PO_4 at the same reaction condition. Comparison of the work related to the use of K_3PO_4 confirms that using the catalyst in powder form typically gives higher biodiesel yields and hence this gives credence to the use of powder form of catalyst in the present work. Biodiesel production from the transesterification of soybean oil in the presence of a heterogeneous catalyst i.e. tri-potassium phosphate in subcritical methanol has also been studied by Yin et al. [16]. The results showed that tri-potassium phosphate exhibits high catalytic activity for the transesterification of soybean oil. The effects of reaction variables, including the reaction temperature, the molar ratio of oil to methanol, the catalyst amount, and the water and oleic acid content in the soybean oil, on the yield of fatty acid methyl ester (FAME) biodiesel were systematically investigated. It was reported that under the optimal conditions of temperature as 65 °C and methanol to oil molar ratio as 24:1, 95.6% yield of the FAME was obtained in 30 min with loading of 1 wt% K_3PO_4. K_3PO_4 gave higher biodiesel yield as compared to other catalysts. A detailed comparison with literature indicates that in accordance with the results obtained in the present work, tri potassium phosphate can be considered as the more effective heterogeneous catalyst for the biodiesel production from waste cooking oil and hence was used in the remaining set of experiments related to the effect of operating parameters.

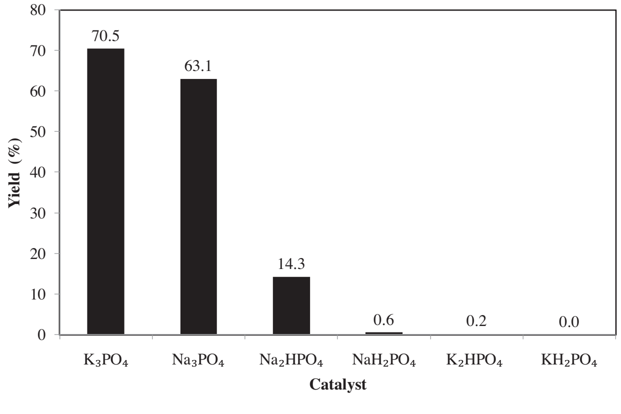

Fig. 4. Effect of catalyst on the yield of biodiesel. [Reaction conditions: OMMR = 1:6; catalyst concentration = 2% (by wt of oil); temperature = 60 °C; duration = 120 min.]

3.2. Effect of catalyst loading

The effect of catalyst loading on the transesterification reaction of WCO has been investigated over a range of 1–4% (by weight based on the WCO). Experiments were performed at oil to methanol molar ratio of 1:6 and temperature of 60 °C. The obtained results have been depicted in Fig. 5. It can be seen from the figure that an increase in the catalyst concentration from 1 to 3% results

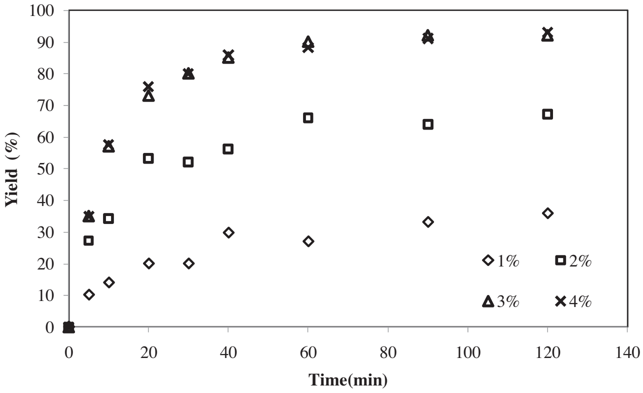

Fig. 5. Effect of catalyst concentration on the yield of biodiesel. [Reaction conditions: OMMR = 1:6; catalyst = K_3PO_4; temperature = 60 °C.]

in an increase in the biodiesel yield from 36 to 93%, however, a further increase in the catalyst concentration from 3 to 4 wt% does not show a significant increase in the biodiesel yield. Thus it can be concluded that the catalyst concentration of 3% by weight of oil is optimum for the transesterification reaction of waste cooking oil with methanol. An initial increase in the catalyst loading represents increase in the catalyst activity and hence biodiesel yield increases till an optimum loading. However, further increase in catalyst loading beyond the optimum value has no effect on biodiesel yield irrespective of excess catalyst activity and hence any excess use of the catalyst must be avoided so as to minimise the separation requirements.

Yin et al. [16] also investigated the effect of the catalyst loading on the progress of transesterification reaction by varying the amount of K_3PO_4 from 0 to 1% by weight of oil, while keeping the reaction temperature constant at 220 °C and the molar ratio of methanol to oil at 24:1. It has been reported that there was no reaction at 220 °C in the absence of K_3PO_4. When the amount of K_3PO_4 was increased from 0.5 to 1.0 wt%, the yield of FAME at 30 min was enhanced from 45 to 100%. Viola et al. [15] investigated biodiesel synthesis from fried vegetable oils via transesterification reaction using heterogeneous catalyst such as CaO, SrO and K_3PO_4. Experiments were performed at oil to methanol molar ratio of 1:6, temperature of 65 °C, stirring speed of 800 rpm and reaction time of 3 h at different catalyst loadings. It was reported that for all the catalysts studied, biodiesel yield increased from 91 to 93% in the case of CaO, 84 to 86% in the case of SrO and 65 to 85% in the case K_3PO_4 respectively when the catalyst concentration was increased from 1.5 to 10% (by wt). Based on the results obtained in the present work and subsequent comparison with the literature, it can be established that it is important to use an optimum catalyst concentration so as to get the maximum benefits at the same time not introducing significant load on the downstream processing steps. A comparison of the current work with the literature also establishes that the optimum loading of the catalyst is indeed dependent on the specific system under question and needs to be established using laboratory scale investigations.

3.3. Effect of methanol molar ratio

The optimisation of oil to methanol ratio is again important in order to reduce the utility requirement in the downstream processing step of methanol recovery. According to the transesterification reaction, 3 mol of methanol are required for reaction with 1 mol of oil to yield 3 mol of fatty alkyl ester and 1 mol of glycerol. As transesterification reaction is reversible in nature, methanol to oil ratio should be more than stoichiometric requirement in order to shift the equilibrium towards the product side. The transesterification was carried out using 1:8, 1:6, and 1:4 molar ratios of oil to methanol with the catalyst (K_3PO_4) quantity being kept constant at a concentration of 3% by weight and temperature of 60 °C. The obtained results in terms of biodiesel yield under different molar ratios have been shown in Fig. 6. It can be seen that the biodiesel yield increased from 58 to 93%, as oil to methanol molar ratio increased from 1:4 to 1:6. However a further increase in the oil to methanol ratio to 1:8 had no significant influence on the biodiesel yield and the observed biodiesel yield at molar ratio of 1:8 was slightly less as compared to the 1:6 molar ratio. The obtained result can be attributed to the fact that the use of significantly higher molar ratio results in diluted products of biodiesel and glycerol which might initiate the reverse reaction to reduce the effective yield. Therefore based on the present work, the appropriate oil to methanol ratio of 1:6 for the transesterification reaction of waste cooking oil with methanol has been recommended.

Dehkordi et al. [9] investigated transesterification of waste cooking oil using Ca and Zr mixed oxides as heterogeneous base catalysts. It was reported that an increase in the oil-methanol molar ratio over the range of 1:3–1:60 resulted in an increase in the biodiesel yield from 22.7 to 92.1% for the catalyst loading of 10 wt%. Alves et al. [17] studied transesterification of waste frying oil (WFO) with methanol and ethanol in a batch reactor using a zinc aluminate catalyst prepared by the combustion reaction method. Influence of the oil: alcohol molar ratio on the biodiesel yield over the range of 1:6–1:65 was studied at 200 °C and it was reported that the molar ratio of WFO: alcohol of 1:40 is the optimum for the transesterification of WFO, either with methanol or ethanol. The optimum molar ratio established in the present work is much lower than the other literature illustration which is significant design aspect, considering the fact that methanol recovery is the highest energy consuming step in the entire transesterification process.

3.4. Effect of temperature

The effect of reaction temperature on the biodiesel yield has been investigated over a temperature range of 30–60 °C under the fixed conditions of reactant molar ratio and catalyst loading (1:6 of OMMR and 3 wt% catalyst concentration). The obtained results have been presented in Fig. 7 which indicate that with an increase in temperature from 30 to 50 °C, a corresponding increase in the biodiesel yield from 54 to 92% is observed whereas a further increase in the reaction temperature from 50 to 60 °C results only in a marginal increase in the biodiesel yield from 92 to 93%.

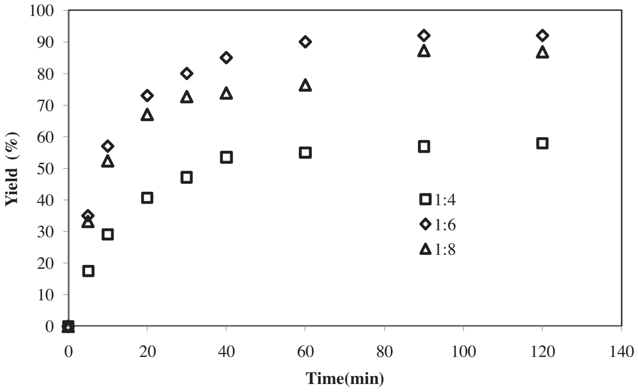

Fig. 6. Effect of oil to methanol molar ratio on the yield of biodiesel. [Reaction conditions: catalyst = K_3PO_4; catalyst concentration = 3% (by wt of oil); temperature = 60 °C.]

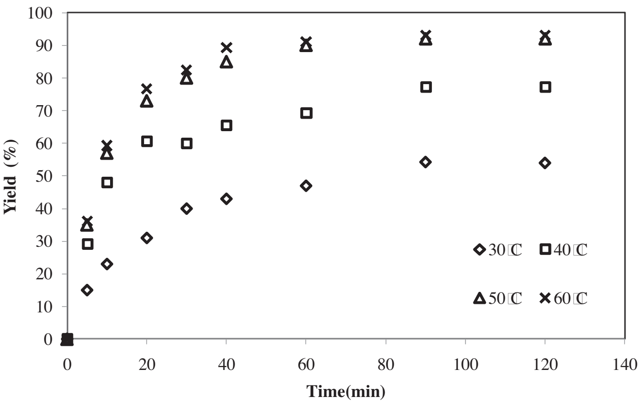

Fig. 7. Effect of temperature on the yield of biodiesel. [Reaction conditions: catalyst = K_3PO_4; OMMR = 1:6; catalyst concentration = 3% (by wt of oil).]

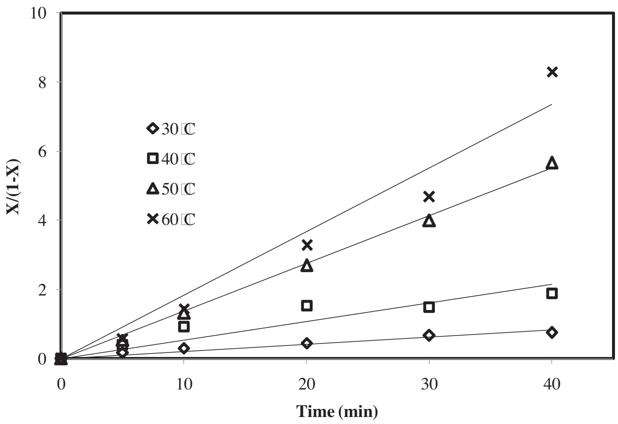

Fig. 8. Kinetic study for establishing the rate constants.

Table 2
Rate constants and activation energy.

Temperature (°C)	Rate constant (k) (L/mol min)	Correlation factor R^2	Frequency factor (k_0) (L/mol min)	Activation energy (kJ/mol)
30	0.02	0.95	2.95×10^9	64.241
40	0.05	0.83		
50	0.14	0.99		
60	0.18	0.96		

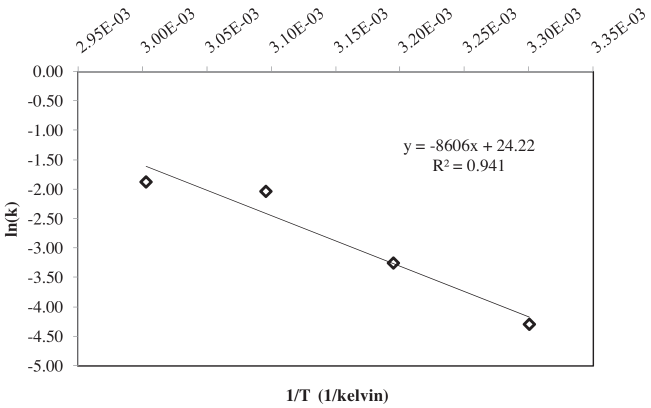

Fig. 9. Arrhenius plot for estimation of activation energy.

The obtained results can be attributed to the enhanced solubility of methanol in oil phase with an 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 significant effect on the final conversion to ester which can be also attributed to lower extent of cavitational effects at higher operating temperatures contributing in a negative manner. It is also important to note here that higher temperatures below the optimum also decrease the time required to reach the maximum conversion. Rahayu et al. [18] investigated effect of reaction temperature from 30 to 60 °C for biodiesel production from coconut oil using heterogeneous solid catalyst as tri-potassium phosphate at catalyst loading of 4% by weight of oil, stirring speed of 500 rpm and equilibrium reaction time of 20 min. It was reported that oil conversion to biodiesel increased from 73.2 to 99.3% with an increase in the reaction temperature from 30 to 60 °C.

3.5. Reaction kinetics

The obtained data for the biodiesel yield at different temperatures has been shown in Fig. 7 for oil to alcohol molar ratio of 1:6, catalyst concentration of 3% and percentage amplitude of 50% (i.e. 375 W supplied power). The data has been analysed using second order kinetics model to determine the kinetic constants at different temperatures. The consideration of irreversibility of this reaction is favoured with an excess of methanol that induces limiting 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, 50 and 60 °C and the obtained kinetic constants from these plots have been given in Table 2. It has been observed that the rate constant for transesterification reactions increased from 0.02 to 0.20 L/(mol min) with an increase in the temperature from 30 to 60 °C. Similar kinetic study for the transesterification of palm oil in the presence of heterogeneous catalyst in ultrasound assisted system has been reported by Salamatinia, et al. [12] at different reaction temperatures. It has been reported that rate constant for each reaction step (i.e. triglyceride to diglyceride, diglyceride to monoglyceride and monoglyceride to glycerol) increased with an increase in temperature of the transesterification reaction from 55 to 65 °C. Also, the reaction rate constant was higher for monoglyceride to glycerol (1.58 L/(mol min)) transformation as compared to triglyceride to diglyceride (0.85 L/(mol min)) and diglyceride to monoglyceride (0.93 L/(mol min)) transformation. Kinetic studies of WCO conversion to biodiesel in the presence of heterogeneous catalyst as heteropoly acid have been reported by Talebian-Kiakalaieh et al. [19] under optimum conditions of 70:1 molar ratio of methanol to oil, 10 wt% catalyst loading and 14 h of reaction time. It has been reported that reaction rate constant increased from 0.059 to 0.1062 min^{-1} as the temperature of the transesterification reaction increased from 50 to 70 °C.

The dependence of the forward reaction rate constant on the temperature is described by Arrhenius law, as given in Eq. (4). The activation energy can also be obtained using rate constant data for the controlled temperature experiments. A satisfactory linear coefficient of 0.96 was obtained for the data fitting performed in the present work. The slope of the straight line fitting depicted in Fig. 9 can be applied to estimate the activation energy. The obtained result is shown in Table 2 with the activation energy estimated to be 64.241 kJ/mol and the pre-exponential factor was found to be 2.95×10^9 L/(mol min). Salamatinia et al. [12] investigated kinetic aspects of transesterification of palm oil using heterogenous catalyst as strontium oxide using low frequency ultrasonic irradiation (20 kHz, 200 W) and reported that activation energies varied between 70.63 kJ/mol and 136.93 kJ/mol. Vyas et al. [20] reported activation energy of 112.86 kJ/mol for transesterification of Jatropha oil with methanol in a heterogeneous system, using alumina loaded with potassium nitrate as a solid base catalyst. It was found that the activation energy obtained in the present work was lower than that observed for other systems, which can be attributed to high catalytic activity of the catalyst used in the present work that can greatly lower the activation energy. Also the cavitational effects, mainly in terms of the intense levels of turbulence and mixing generated in the reactor contribute to the lowering of this apparent activation energy. The physical effects contribute to the intensification because of the generation of microemulsions between the two phases taking part in the reaction, increasing the available interfacial area enormously and giving faster reaction rates.

3.6. Catalyst reusability

Catalyst reusability is one of the important factors for economical operation of transesterification of waste cooking oil with methanol using heterogeneous catalyst, as this can allow reduction in the operating cost. After first run, catalyst used for the transesterification reaction of waste cooking oil was removed from the reaction mixture by filtration. The filtered catalyst was reused after activation treatment involving methanol wash followed by washing using aqueous solution of KOH. After treatment, catalyst was reused for the next seven to eight runs with the same reaction parameters which were used for fresh catalyst assisted transesterification of WCO with methanol. The result of catalyst reusability study has been depicted in Fig. 10 and it was found that almost similar conversion can be obtained up to fourth run i.e. biodiesel yield only marginally decreased from 92 to 90%. After the fifth run, catalyst activity started decreasing significantly and the biodiesel yield of 65% was obtained in eighth run. The obtained result can be attributed to the fact that that K_3PO_4 is converted to K_2HPO_4 and KH_2PO_4 during the transesterification reaction, due to the reaction with methanol [21] or there can be a reduction in active sites of the catalyst due to agglomeration or sintering effects in the later cycle of transesterification process [14]. Similar, catalyst reusability study has been reported by Jiang et al. [22] for transesterification of rapeseed oil with methanol using heterogeneous catalyst as trisodium phosphate. The optimum operating conditions as temperature of 343 K, mass ratio of catalyst to oil as 3%, molar ratio of oil to methanol as 1:9, rotation speed of 400 rpm and reaction time of 2 h were determined by a detailed study of operational parameters employed in the reactor. Under these conditions good activity of catalyst even after eighth run was reported with biodiesel yields of around 93% in each run. Catalyst reusability of three solid catalysts such as CaO, SrO and K_3PO_4 have been investigated by Viola et al. [15] for the transesterification of fried oils with methanol. It was reported that there is a marginal loss in the efficiency of catalyst with a reduction of biodiesel yield equal to 14% for CaO, 22% for SrO and 12% for K_3PO_4. The obtained reduction in the activity was attributed to the fact that product glycerol remains adsorbed on the catalyst surface.

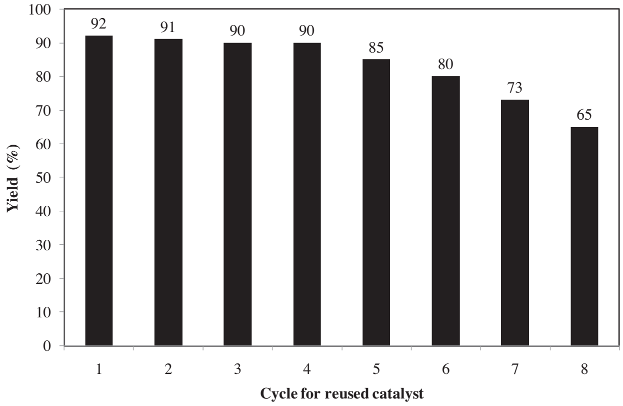

Fig. 10. Catalyst reusability [reaction conditions: catalyst = K_3PO_4; OMMR = 1:6; catalyst concentration = 3% (by wt of oil); temperature = 50 °C].

3.7. Comparison between acoustic and conventional method

The optimised operating parameters for the operation using ultrasound irradiation were used for the conventional stirring operation and the obtained results have been shown in Fig. 11. It can be seen from the figure that acoustic cavitation results in 92% biodiesel yield whereas conventional stirring results in much lower extent of biodiesel yield as 59% over a similar reaction time. The transesterification reaction is mass transfer controlled process due to the heterogeneous nature (i.e. methanol is immiscible with WCO) of the reaction system. The intensification obtained due to the use of ultrasonic irradiations is attributed to the physical effects of the cavitation phenomena, mainly in terms of the intense levels of turbulence and mixing generated in the reactor. Because of the generation of microemulsions between the two immiscible phases taking part in the reaction, the available interfacial area for the reaction increases enormously, giving faster reaction rates and the requirement of less-severe conditions. Salamatinia et al. [12] studied intensification of biodiesel production process using low frequency ultrasonic irradiation (20 kHz, 200 W) from commercial palm oil, corn oil, canola oil and sunflower oil in the presence of heterogeneous catalyst as SrO. It was reported that ultrasound effectively intensified the biodiesel production process giving biodiesel yield of 97% at a pulsing time of 9 s followed by a gap of 2 s within a reaction time of 30.7 min. Hingu et al. [23] has reported similar result in the case of homogeneous catalyst as KOH using sonication and conventional method with conversion of 89% and 57% in the case of sonication and conventional method respectively. Wang et al. [24] have also reported that the time required for the transesterification reaction is much lower in cavitational reactor as compared to conventional stirring method. Hahn and Dong [25,26] have also reported that ultrasound enhances the effective emulsification and mass transfer in the reaction mixture giving higher ester formation in less time as compared to

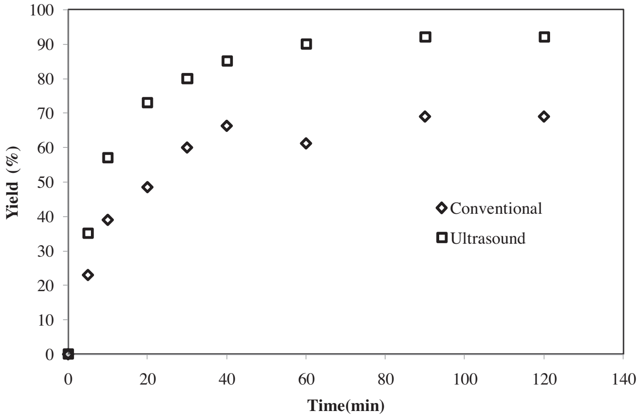

Fig. 11. Comparison of biodiesel yield in the ultrasound assisted and conventional methods. [Reaction conditions: catalyst = K_3PO_4; OMMR = 1:6; catalyst concentration = 3% (by wt of oil); temperature = 50 °C; ultrasound method: percentage amplitude = 50%; conventional method: stirrer speed = 1000 rpm.]

Table 3
Biodiesel properties.

Property	Conventional	Ultrasound	ASTM D6751
Density, g/cm^3	0.887	0.879	0.86–0.9
Kinematic viscosity, 40 °C, mm^2/s	3.76	3.82	1.9–6.0
Flash point, °C	190	161	130 min
Pour Point, °C	3	1	−5 to 5
Acid value, mg of kOH/g of oil	0.82	0.32	0.5 max

conventional stirring method. Deshmane et al. [27] have also confirmed the observed intensification due to the use of ultrasound with conversion of about 95% being achieved in 150 min at 40 °C as compared to a conversion of 93% in 300 min for the conventional approach at same temperature.

3.8. Biodiesel properties

The biodiesel properties such as density, flash point, pour point, kinematic viscosity, and acid value of the final dried product obtained under optimum conditions of oil to methanol molar ratio of 1:6, catalyst concentration of 3% by wt of oil and reaction temperature of 50 °C using ultrasound and conventional methods are shown in 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 depends on the quality of separation of the triglyceride/glycerine from the product, fatty acid methyl esters. The flash point of the biodiesel synthesized from ultrasound (155 °C) was observed to be lower than that obtained using the conventional method (190 °C) which can be attributed to higher purity of the final product. The obtained results can be explained on the basis of the presence of unreacted triglyceride and fatty acid in final reaction mixture obtained using conventional stirring based approach attributed to lower efficiency of the separation. As biodiesel yield in conventional method is very less (59%) compared to the ultrasound method (92%), it is possible that in the case of conventional method, the presence of unreacted triglyceride and fatty acid in final reaction mixture is on a higher side as compared to ultrasound method. Hence there is a variation in flash point and acid value for conventional and ultrasound method. Similar results for the biodiesel properties have been reported for the transesterification of waste vegetable oil using an aluminium hydrogen sulphate [28] and calcium oxide [15] as a heterogeneous solid catalyst.

4. Conclusions

The present work has clearly illustrated the applicability of heterogeneous catalyst for the production of biodiesel in ultrasound assisted transesterification of waste cooking oil with methanol under ambient operating conditions. K_3PO_4 showed good catalytic activity in terms of higher biodiesel yield as compared to other catalysts used in the work. Maximum biodiesel yield of 92% has been observed at optimum reaction parameters as oil to methanol molar ratio of 1:6, catalyst loading of 3% by weight and reaction temperature of 50 °C. Catalyst K_3PO_4 can be effectively recycled and reused up to four runs with negligible loss in the catalyst activity. Comparison of sonication method with conventional stirring method has enabled to clearly illustrate the role of ultrasonic field in increasing emulsification and mass transfer in reaction mixture giving higher biodiesel yield. The kinetics of the conversion of triglycerides through transesterification fitted well in a second-order reaction scheme and it was observed that the rate constant increased with an increase in the operating temperature. Use of ultrasound also allows the lowering of the apparent activation energy. The properties of biodiesel produced from both the methods were in accordance with the ASTM standards and the ultrasound based process gave superior properties for the final product.

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