Research Paper

Study of variables affecting the synthesis of biodiesel from Madhuca Indica oil

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Biodiesel derived from non-edible Madhuca Indica oil (MIO) seems to be a better alternative to diesel oil in India. In the present work, effects of reaction variables such as mass ratio of methanol to oil, catalyst concentration, reaction time and reaction temperature on biodiesel yield were studied. The acid value of the commercially available MIO is high, and hence a two-step process was used to produce biodiesel from MIO. In the first step, the acid value of the MIO was reduced to less than 1 mg KOH/g, using acid-catalyzed transesterification. In the second step, the pretreated MIO was converted to biodiesel using alkaline-catalyzed transesterification. From the experimental results, it is observed that the optimized conditions for biodiesel production are a 1 : 4 mass ratio of methanol to oil, 55 °C reaction temperature, 120 min of reaction time, and 1% sodium hydroxide catalyst. The properties of the MIO biodiesel were found to be within the biodiesel limits of the European Union. Hence, the MIO biodiesel can be used as a substitute for diesel for the sustainable development of rural areas and as a renewable fuel.

1 Introduction

During recent years high activities could be observed in the field of alternative fuels, due to the fact that the supply of petroleum fuels strongly depends on a small number of oil-exporting countries. In the years 2004–2005, India imported 75% of its crude oil from other countries to meet the energy requirements. The demand for diesel and gasoline increased drastically in the years 2008–2009. It has been estimated that the demand for diesel will be 66.90 Mt for the years 2011–2012. Biodiesel and alcohol are considered to be supplementary fuels to the petroleum fuels in India. These biofuels are expected to provide employment generation to rural people through the production of vegetable oils and they can be beneficial to sugarcane farmers through the ethanol program [1]. A number of researchers examined the fatty acid profiles of seed oils of 75 plant species having 30% or more

fixed oil in their seeds. They reported that the fatty acid methyl esters of the oils of 26 species were found most suitable for use as biodiesel and that they meet the major specification of biodiesel standards of the USA, Germany and Europe [2].

Mahua is the name of a medium-size to larger tree, *Madhuca longifolia* of the Sapotaceae family, with a wide and round canopy. It is a slow growing species which attains a mean height of 0.9–1.2 m at the end of the fourth year. It may attain a height of up to 20 m. The variety *latifolia* is common throughout the Indian subcontinent. As a plantation tree, mahua is an important plant having vital socio-economic value. This species can be planted on roadsides, canal banks, *etc*., on commercial scale and in social forestry programs, particularly in tribal areas. Drying and decortification yield 70% kernel (based on seed weight). The kernel of the seed contains about 50% oil. The oil yield in an expeller is nearly 34–37% and the fresh oil from properly stored seeds is yellow in color [3]. Figure 1a, b shows the mahua tree and seeds, respectively. The seed and oil potentials of this tree in India are 500 and 180 million tons, respectively, and Table 1 shows the fatty acid composition of the Madhuca Indica oil (MIO) available in different parts of India [4].

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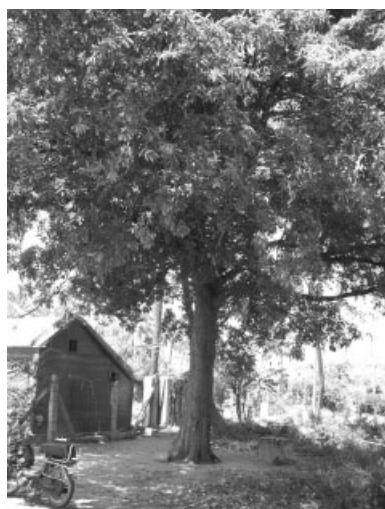
Figure 1. (a) Mahua tree, (b) mahua seeds.

Table 1. Fatty acid composition of MIO.

Fatty acid	Weight [%]
Arachidic	0.00– 3.3
Linoleic	8.9 –13.7
Oleic	41.0 –51.0
Stearic	20.0 –25.1
Palmitic	16.0 –28.2

In a review paper, it has been reported that biodiesel can be produced by the transesterification reaction of triglycerides of vegetable oils with methanol, with the help of basic, acidic and enzymatic catalysts [5]. The important variables that affect the transesterification reaction are the amounts of methanol and sodium hydroxide, the reaction temperature and reaction time. Most researchers have used 0.1–1.2% (by weight of oil) of sodium hydroxide (NaOH) for biodiesel production. If the acid value of the oil is greater than 1 mg KOH/g of oil, then a higher amount of NaOH is required to neutralize the free fatty acids (FFA). The reaction temperature should always be maintained below the boiling point (65 °C) of methanol. The methyl ester conversion rate increases with reaction time and varies from 60 to 180 min.

Different researchers have reported different reaction times for the transesterification process [6–12]. The optimum conditions for the methanolysis of sunflower oil are a 6 : 1 molar ratio of methanol to oil, 50 °C reaction temperature, and 1% NaOH concentration [10]. Researchers developed a two-step transesterification technique to produce biodiesel from vegetable oil having high amounts of FFA [13–16]. The present work was undertaken to study the effect of reaction variables on the transesterification of MIO.

2 Materials and methods

In the present work, methanol was chosen as the alcohol used for the transesterification of MIO, because of its low cost and its physical and chemical advantages (polar and shortest-chain alcohol). From the literature, it was observed that NaOH is a very well accepted and widely used catalyst because of its low cost and high product yield. Methanol of 99.5% purity, sulfuric acid of 99% purity and sodium hydroxide pellets of pure grade were purchased from Merck Chemical Company, India. All other reagents were of analytical grade or higher.

2.1 Extraction of MIO

For the present work, the mahua seeds were collected from rural areas. The seeds were dried in sunlight for 10 days and cleaned manually to remove all foreign matter such as dust, dirt, stones and chaff, as well as immature, broken seeds. Drying and decortification yielded 70% kernel based on seed weight. The kernel of the seed contains about 50% oil. In India, a large rotating pestle and mortar system powered by a motor known as a ghani (Fig. 2) is used for oil extraction from non-edible seeds. The mortar is firmly fixed in the ground whereas the pestle rotates. When the seeds are fed slowly into

Figure 2. Ghani (oil expeller).

the mortar, the pressure exerted by the pestle breaks the cells and releases the oil, which runs out of a small aperture at the base of the mortar. Then, the raw oil is refined by filtering, winterizing, bleaching, degumming and filtering. The crude oil is filtered by filter cloth. In winterizing, the oil is kept at low temperatures, during which higher-melting glycerides crystallize and are separated by filtration. Then, the oil is bleached by the addition of a small amount of activated carbon prior to the final filtration. Then, a small amount of water is added to the oil, in order to remove gums and mucilage that are released along with the oil as the plant cells rupture during extraction. The above treatment, with heat, causes the gums to flocculate, after which they are removed by settling. The filtered and refined oil was heated above 100 °C for 1 h to remove the moisture. Table 2 shows the characteristics of the MIO.

Table 2. Characteristics of MIO.

Property	Value
Acid value [mg KOH/g of oil]	16
Refractive index	1.456
Saponification value [mg KOH/g]	190
Iodine value [g I_2/100 g]	59
Viscosity at 40 °C [mm^2/s]	27.63
Density at 15 °C [kg/m^3]	915
Water content [mg/kg]	93
Color	dark yellow

2.2 Transesterification setup

The transesterification reactions were carried out in a round-bottom flask of 250 mL capacity, equipped with a reflux condenser. The flask was immersed in a constant-temperature bath, which was capable of maintaining the reaction temperature required for the reaction. A hot plate with magnetic stirrer arrangement was used for heating and stirring the mixture. The agitation was set at a constant speed throughout the experiment (300 rpm).

2.3 Two-step transesterification

The MIO had an initial acid value of 16 mg KOH/g of oil, corresponding to an FFA level of 8%, which is far above the 1% limit for a satisfactory transesterification reaction using an alkaline catalyst. The reason is that alkaline catalysts react with the FFA to form soap. Hence, a two-step process was used in which an acid-catalyzed pretreatment was used in the first step to reduce the acid value from 16 to 1 mg KOH/g of oil. In the second step, the pretreated MIO was converted to biodiesel by alkaline transesterification.

2.4 Acid transesterification

Of MIO, 100 g was poured into a flask and heated to 60 °C. A solution of sulfuric acid (1% based on oil weight) in 30 g of methanol was heated to 60 °C and then added to the reaction flask. This mixture was stirred for 120 min. Samples were withdrawn from the reaction mixture every 15 min and the progress of the reaction was monitored by measuring the acid value. The sample was washed with distilled water to stop the reaction and to separate the catalyst and methanol from the oil phase. Finally, the sample was centrifuged for 20 min. The variation of the acid value with respect to the reaction time is shown in Fig. 3. From the figure, we observe that, as the reaction time increases, the acid value decreases. After the reaction, the acid value of the products was lower than 2 mg KOH/g. Then, the product was poured into a separating funnel and was allowed to settle for 2 h. After settling, two layers were observed. The lower layer (treated MIO) was separated for further processing. The top layer containing catalyst and impurities was discarded and the excess methanol was recovered by distillation.
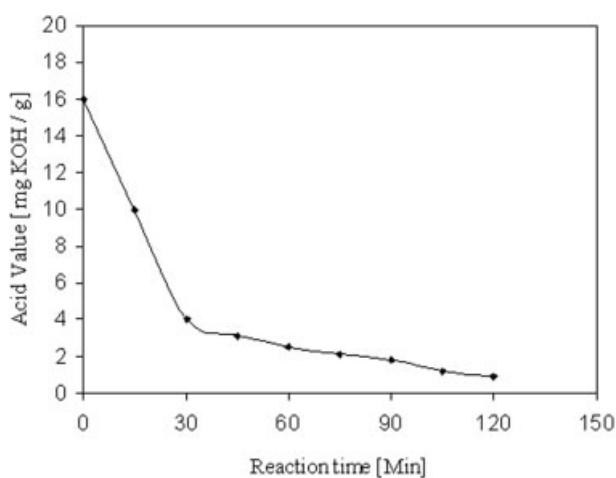

Figure 3. Variation of acid value with reaction time.

2.5 Alkaline transesterification

The acid transesterification setup was used for the alkaline transesterification. The pretreated MIO was heated to the required reaction temperature. The required quantity of sodium hydroxide (NaOH) catalyst was poured into the required amount of methanol and the mixture was stirred until the entire NaOH was dissolved. This sodium methoxide solution was added to the pretreated MIO. The reaction was conducted for the required reaction time. After the reaction, excess methanol was recovered by vacuum distillation and then the product was poured into the separating funnel. The top layer containing esters was washed with warm distilled water (10% by volume), to wash out impurities like soap and

other residues. Finally, the wet methyl esters were heated above 100 °C, to remove the moisture.

2.6 Analytical methods

The acid value of the samples was determined by titration technique (ISO 660-1996). A standard solution of 1 mol KOH solution was used. A weighed amount of the sample was dissolved in a mixed solvent (diethyl ether/95% (vol/vol) ethanol, 1 : 1 mixture by volume) and titrated with an ethanolic solution of KOH. Phenolphthalein was used as indicator. The amount of KOH consumed was registered and the acid value was calculated using the following equation:

$$\text{Acid value} = (56.1 \times V \times C)/m$$

where V is the volume of the KOH solution used for titration (mL), C is the concentration of alcoholic KOH solution (mol/L), and m is the mass of the sample (g).

The monoglyceride, diglyceride and triglyceride contents of the biodiesel were determined using GC in accordance with EN 14105. The biodiesel yield after the post-treatment stage, relative to the amount of MIO poured into the reactor, was calculated from the weights of the methyl esters of MIO and MIO. The properties of the biodiesel were determined as per ASTM standards. The flash point (ASTM D 93-02 a) was determined by a Pensky Martens closed-cup tester and the pour point was determined according to ASTM D 97-02. The kinematic viscosity (ASTM D 445-03) was determined using a Redwood viscometer; the density (ASTM D4052-96) was determined using a relative-density bottle. The calorific value (ASTM D 240-03) was determined using a bomb calorimeter, and the ash content (ASTM D 482-74) was determined using a muffle furnace. The water content (ASTM D 95-990) was measured using a Dean and Stark apparatus. This equipment was supplied by M/s IndLab Equipments, Bangalore, India. All analyses were performed with three replications.

3 Results and discussion

Biodiesel was prepared from non-edible MIO and the effects of the reaction parameters on the biodiesel yield were studied and are discussed below.

3.1 Effect of mass ratio of oil to methanol

The mass ratio of alcohol to vegetable oil is one of the most important variables that affect the biodiesel yield as well as the production cost of biodiesel. The variation of the biodiesel yield with respect to the mass ratio of oil to methanol at different reaction times, reaction temperatures and catalyst amounts is shown in Fig. 4. From the figure, it is observed that the biodiesel yield reaches the highest value at a mass ratio of
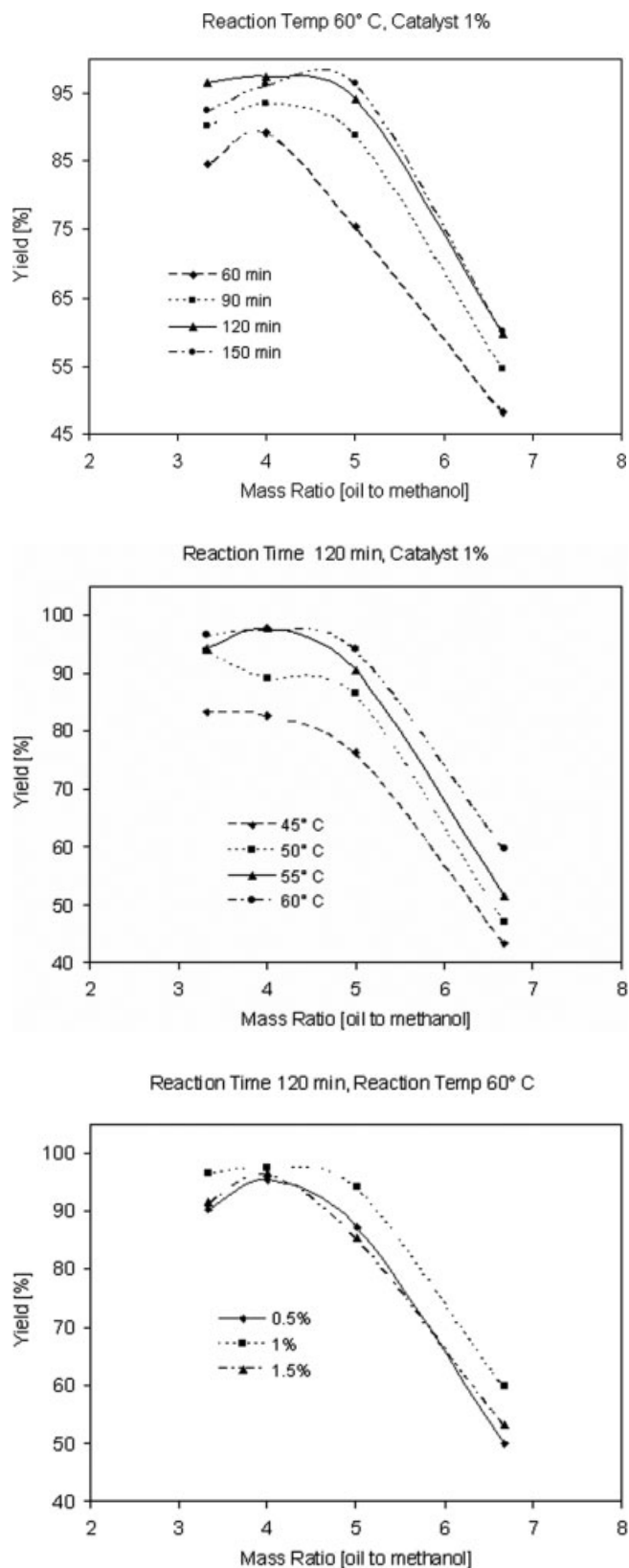

Figure 4. Variation of yield with mass ratio.

4 : 1 and decreases at higher mass ratios of oil to methanol. The results clearly indicate that the optimum mass ratio of oil to methanol required for effective transesterification of MIO is 4 : 1. Moreover, it was found that, when the concentration of methanol was increased above or decreased below the optimum, there was no significant increase in biodiesel production, but the excess or shortfall in concentration of methanol only contributed to an increased formation of glycerol and emulsion. These results agree with those obtained by Encinar [17] who indicated that an excess of alcohol will increase the biodiesel yield by shifting the equilibrium to the product side, but a higher amount of alcohol interferes with the separation of glycerin because there is an increase in solubility.

3.2 Effect of NaOH concentration

The concentrations of the catalyst NaOH adopted in this study were 0.5, 1.0 and 1.5% (based on oil weight). The variation of the biodiesel yield with respect to the catalyst amount is shown in Fig. 5. From the figure, we can observe that the optimum concentration of NaOH required for effective transesterification was 1%. It was observed that, when the NaOH concentration was decreased below or increased above the optimum, there was no significant increase in biodiesel production, but there was increased formation of glycerol and emulsion.

3.3 Effect of reaction temperature

Since the viscosity of the raw MIO was high, the reaction temperatures adopted in this study were 45, 50, 55 and 60 °C. The reaction temperature should always be below the boiling point (65 °C) of methanol and so the reaction temperature was limited up to 60 °C. Figure 6 shows the variation of the biodiesel yield with respect to the reaction temperature. From the figure, it is observed that the ester yield proportionately increased with the increase in reaction temperature. The results clearly indicate that maximum biodiesel yield can be obtained at either 55 or 60 °C. Since the heat required for the temperature rise up to 55 °C is less than that for 60 °C, the reaction temperature of 55 °C is preferred over 60 °C.

From Fig. 6a–c, it is observed that the maximum biodiesel yield was obtained at a reaction temperature of 55 °C, a catalyst amount of 1%, a mass ratio of oil to methanol of 4 : 1, and a reaction time of 120 min.

3.4 Effect of reaction time

In order to optimize the reaction time, the different reaction times selected for this study were 60, 90, 120 and 150 min. The results clearly indicate that the biodiesel yield increased with the reaction time. But a reaction time of 150 min results in darkening of the biodiesel due to the prolonged heating. The variation in reaction time *versus* ester yield percentage is
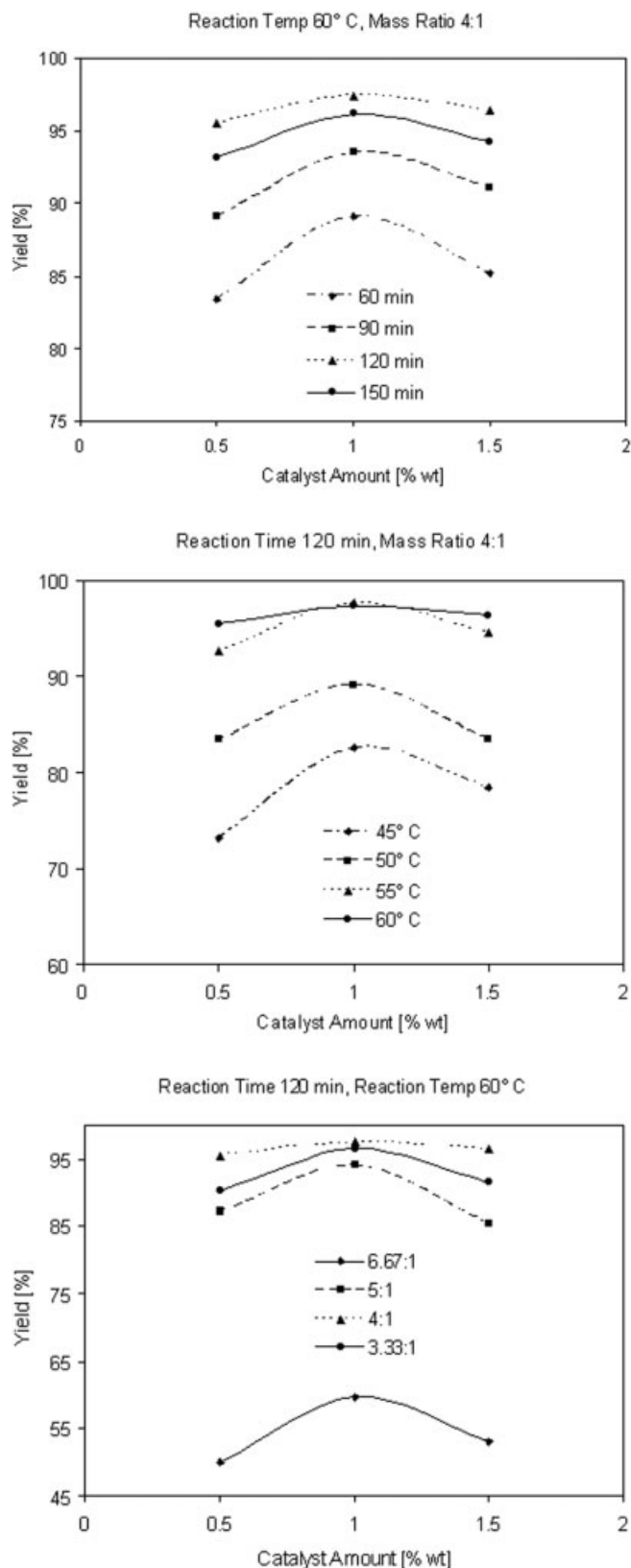

Figure 5. Variation of yield with catalyst amount.

Catalyst Amount 1% (wt), mass ratio 4:1

- ♦- 60 min
- ■- 90 min
- ▲- 120 min
- ●- 150 min

Reaction Time 120 (min), Catalyst 1 % (wt)

- ♦- 6.67:1
- ■- 5:1
- ▲- 4:1
- *- 3.33:1

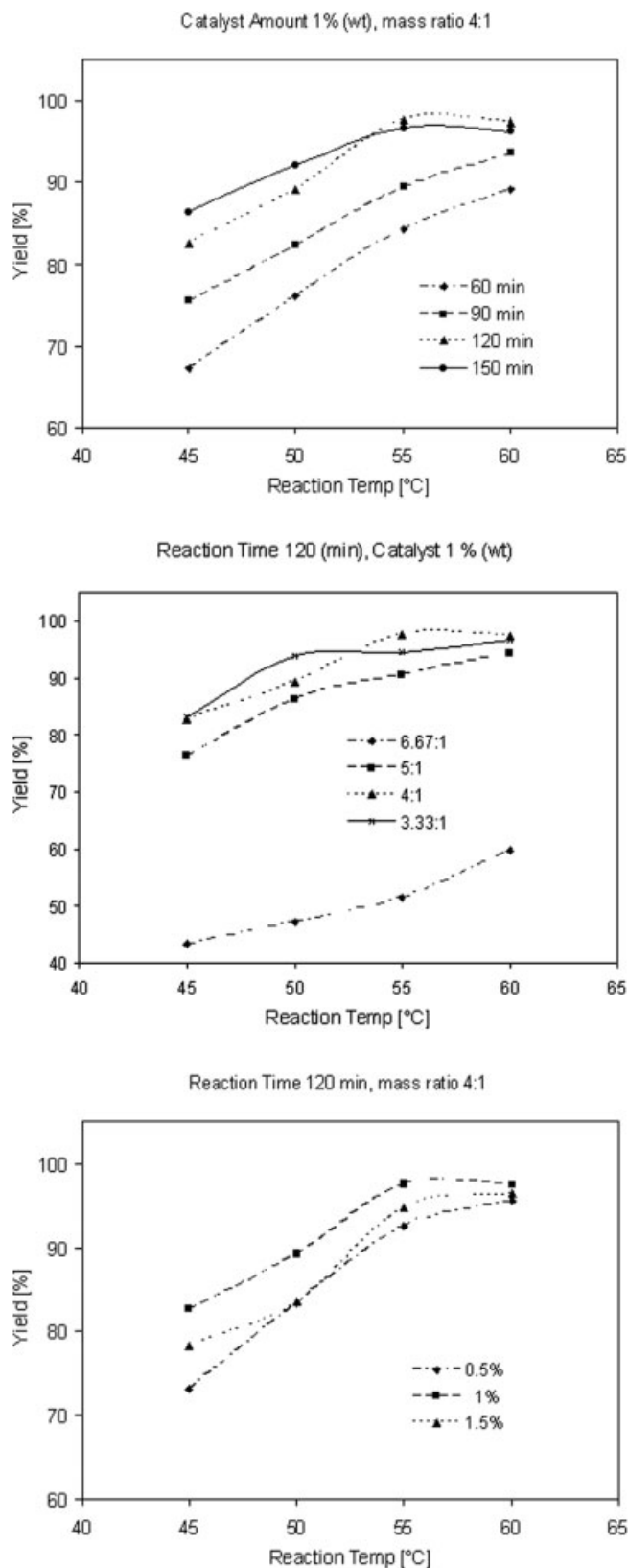Reaction Time 120 min, mass ratio 4:1

- ♦- 0.5%
- ■- 1%
- ▲- 1.5%

Figure 6. Variation of yield with reaction temperature.

shown in Fig. 7. The figure clearly shows that maximum bio-diesel yield can be obtained at 120 min of reaction time. This may be due to the increase in mixing and dispersion of the methanol in the oil phase with reaction time, which is in accordance with the work of Freedman *et al.* [8].

3.5 Properties of the fuel

The important properties of the MIO biodiesel were determined and are shown in Table 3. All the properties of the MIO biodiesel were found to be within the limits of the biodiesel specifications of EN 14214. The decrease in kinematic viscosity from 27.63 to 4.85 mm^2/s is the most important fuel property of the MIO biodiesel. This indicates that the ability of the raw MIO to flow is increased to a significant extent by transesterification. This increase in the ability of the fuel to flow would induce complete burning of the fuel without any ignition delay. The calorific value of MIO biodiesel is lower than that of diesel due to the presence of oxygen in its molecular structure.

Table 3. Properties of MIO biodiesel.

Property	MOME	EN 14214 (limits)
Flash point [°C]	129	>120
Pour point [°C]	5	–
Calorific value [kJ/kg]	36914	–
Kinematic viscosity at 40 °C [mm^2/s]	4.85	3.5–5.0
Density at 15 °C [kg/m^3]	883	860–900
Cetane number	51	>51
Acid value [mg KOH/g]	0.42	<0.5
Iodine value [g I_2/100 g]	110	<120
Water content [mg/kg]	138	<500
Free glycerin [wt-%]	0.02	<0.02
Monoglycerides [wt-%]	0.6	<0.8
Diglycerides [wt-%]	0.2	<0.2
Triglycerides [wt-%]	0.1	<0.2

4 Conclusions

Two-step transesterification is an effective way of converting MIO containing high amounts of FFA to biodiesel. From the experimental results, it is observed that the optimized conditions for biodiesel production are a 4 : 1 mass ratio of oil to methanol, 55 °C reaction temperature, 120 min of reaction time, and 1% NaOH catalyst, resulting in a biodiesel yield of 97.6%. The fuel properties of MIO biodiesel were found to be comparable to those of diesel and to conform to the EN biodiesel standards. A higher mass ratio of methanol to oil, lower reaction time, lower reaction temperature and higher catalyst amounts result in higher emulsion, which increases the viscosity and leads to the formation of a gel. Use of MIO for
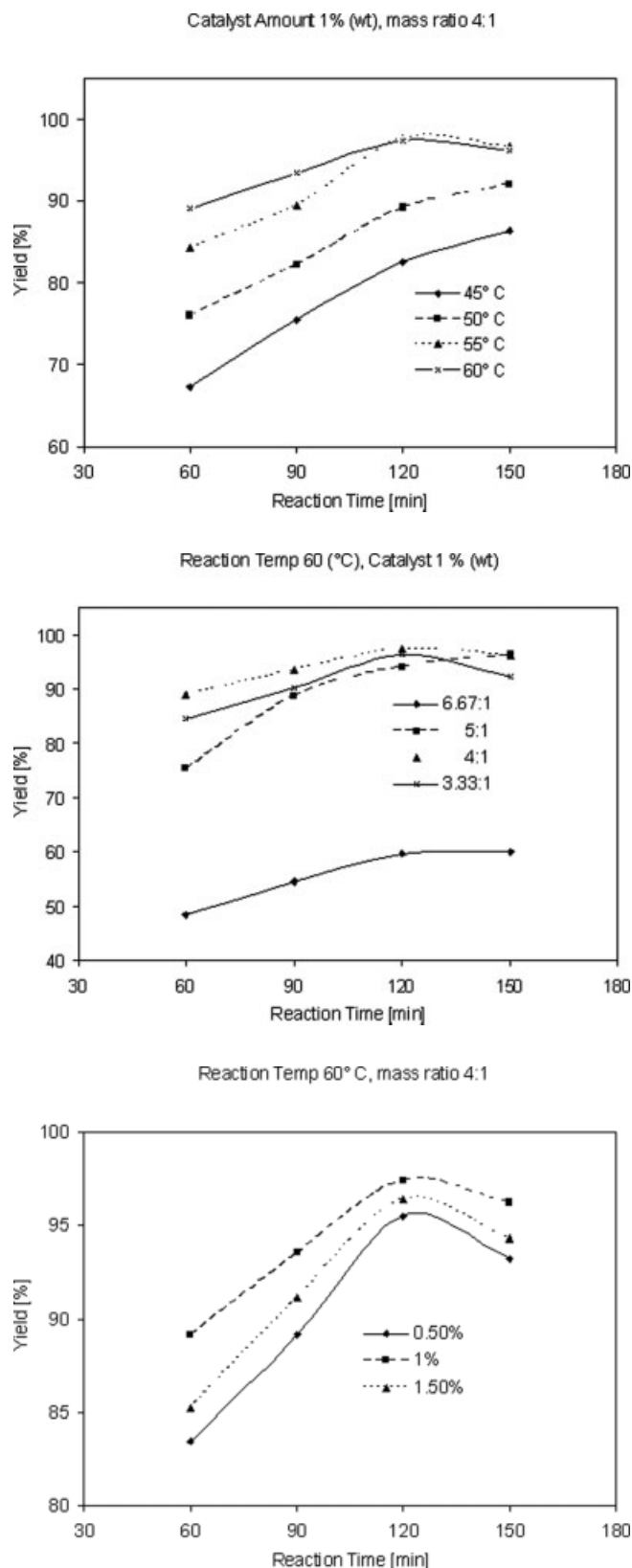
Figure 7. Variation of yield with reaction time.

biodiesel production will improve the rural economy and is beneficial for the energy supply of India.

Acknowledgment

The conflict of interest statement

The authors have declared no conflict of interest.

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