Research Article

Biodiesel Production from Mahua Oil by using Two-Step Trans-esterification Process

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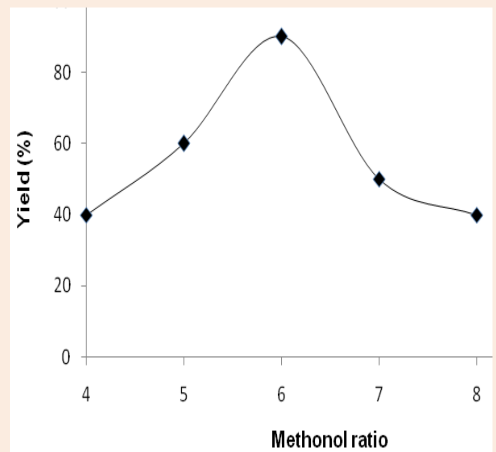
Abstract
At present, the biodiesel is produced in large scale from the refined edible type oils using methanol and an alkaline catalyst. In India large amount of non-edible type oils and fats are available. The difficulty of these oils in biodiesel production is that they have higher percentage of free fatty acids (FFA). These free fatty acids are major obstacle while reacting with the alkaline catalyst resulted in production of soaps that inhibit the production and separation of biodiesel. Based on this strategy, non edible oil *Mahua* (Karanja) was chosen for this investigation. The maximum conversion efficiency of 90% of Mahua oil biodiesel yield was achieved under optimized conditions of 0.5 wt% acid catalyst concentration and 0.4% concentration of NaOH with respect to 6:1 oil to molar ratio and 60 minutes of reaction time with 60 ± 1 °C temperature.



Key words: Biodiesel, High free fatty acid, Mahua oil, two step trans-esterification.

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Introduction

All over the world there is a severe demand for fuel mainly due to the increased usage as well as parallel depletion of fossil fuel resource. The net energy demand is expected to increase at 4.8% per year. Increased consumption of fuels has resulted in increased release of green house gases into the atmosphere. The diminishing petroleum reserves and the deleterious effects of exhaust gases from petro and petro derived products have forced us to search for new alternative sources. Various alternative fuel options explored include biogas, producer gas, ethanol, methanol and biodiesel [6]. Among renewable energy resources biodiesel has received more attention during the past few years. Biodiesel has many merits as a renewable energy resource that includes renewable, biodegradable and non-toxic. Biodiesel is considered as carbon neutral fuel. Other environmental advantages of biodiesel include no net emission of sulfur oxide. Compared with petro-diesel, biodiesel has a more favorable combustion emission profile such as low emission of carbon monoxide, particulate matter and unburned hydrocarbons. Biodiesel is produced from India by utilizing its vast agricultural resources which offers a clean substitute for expensive fossil fuel import. The main commodity sources for biodiesel in India are Mahua (*Madhuca India*), Sal (*Shorea robusta*), Neem (*Azadirachta indica*), Karanja (*Pongamia pinnata*), Kusum (*Schleichera deosa*) and Ratanjyot (*Jatropha curcus*) [13].

Recently, environmentalists have commented on the potential negative impact of biodiesel production from edible oils leading to deforestation and destruction of ecosystem. In other words, the limited land that has been used to grow food would instead be used to produce fuel and biodiesel crops. Another related factor, production cost, has also contributed to the limited adoption of biodiesel. The present study focuses on the biodiesel production from non edible oil of *Mahua* (Karanja) and effect of different parameters such as acid, alkali, methanol oil molar ratio, reaction time and temperature on production of biodiesel.

Materials and methods

Biodiesel production (transesterification reaction)

Free fatty acid (FFA) value of oil plays key role in the transesterification process. If free fatty acid content of the oil is lower than 3%, single stage process (alkali transesterification) is will be carried out. If it is greater than 3%, double stage process (acid esterification and alkali transesterification) will be carried out.

Acid catalyzed esterification process

100ml of oil (FFA>3%) was taken in clean conical flask. The moisture content of the given oil was removed by heating the oil at 80°C for 1 hour in magnetic stirrer. After cooling, 30ml of methanol and sulphuric acid was added (volume of H_2SO4 = FFA value x 0.05). It was continuously stirred for 1 hour at 65°C. This mixture was separated for overnight. Top layer consisting of acid esterified oil and bottom layer known as residues were found. The bottom residues layer was separated out from acid esterified oil and used it for biodiesel production.

Alkali catalyzed transesterification process

The bottom layer product of acid esterification was preheated to remove moisture content before starting the reaction. The alkali methanol mixed solution was added to preheated product of the acid esterification. The reaction was conducted at 50 ± 1 °C for 60 min. The resulted product was allowed to settle down under gravity for 8 h in a separating funnel. The products of the alkali transesterification process result in the formation of two layers viz., an upper layer containing biodiesel (methyl ester) and lower layer containing glycerol.

$$\text{Yield of methyl ester (\%)} = \frac{\text{Methyl ester produced (g)}}{\text{Oil taken for the reaction (g)}} \times 100 \qquad (1)$$

(Ref: *National Renewable Energy Laboratory – Biodiesel Analytical Methods 2004*)

Purification

The product was washed with double distilled water to remove the unreacted alcohol, catalyst or glycerol present in the biodiesel. Further the water washed fuel was heated to 110° C in an open container until there was no more steam in the fuel. The resultant fuel should be a clear liquid.

Results and discussion

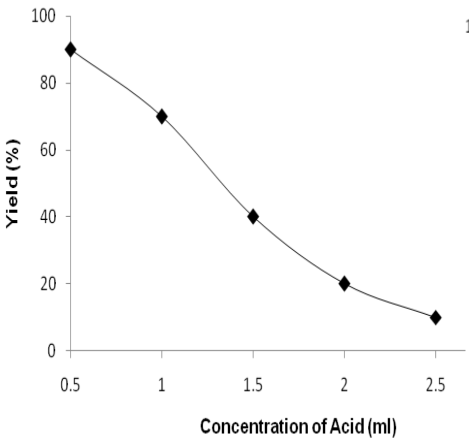
Table 1 The physico-chemical properties of the Mahua oil

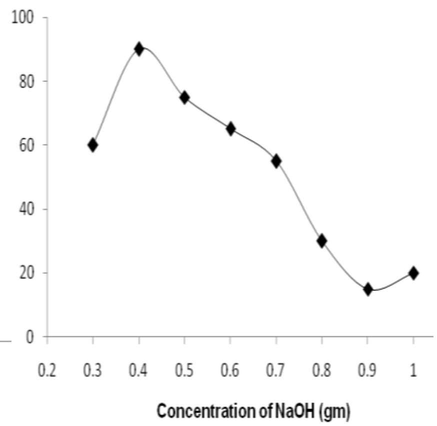
Parameter	**Value**
Moisture (%)	0.016
Free fatty acid (%)	10
Acid value (mg of NaOH/g)	20
Iodine value (gram of iodine /100g)	78.12
Saponification value (mg of KOH/g)	196
Viscosity 40°c (mm^2/s)	55.03

Source: ASTM methods

Effect of acid concentration on biodiesel yield

The sulfuric acid catalyst amount was varied in the range of 0.25–2.5 wt%. The volume of the oil used for the acid esterification reaction. The yield of biodiesel was affected by the amount of catalyst as shown in Fig.1. The acid catalyst process attained maximum esterified oil yield of 85% for 0.5 wt% catalyst concentration. It has been observed in the present experiments that addition of excess sulfuric acid darkens the color of the product but yield remains the same for oil.





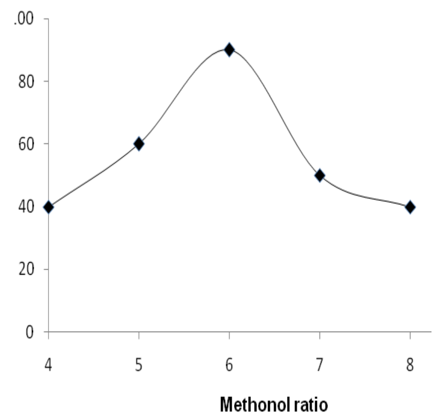


Fig 1 Effect of acid on esterification yield

Fig 2 Effect of alkali on biodiesel yield

Fig 3 Effect of methanol:oil ratio on biodiesel yield

Effect of alkali concentration on biodiesel yield

Transesterification of oil was carried out with NaOH as a catalyst at a concentration of 0.3–1% (w/w oil). Fig.2. shows the yield of biodiesel versus NaOH concentration. The lower catalytic concentration of 0.3% NaOH was insignificant to catalyze the reaction to completion. It was found that the biodiesel yield increased as the amount of catalyst concentration increased from 03% to 0.4% in this study. With the increase in the concentration of catalyst i.e., beyond 0.4%. NaOH, there was decrease in the yield of biodiesel. This is in accordance with the result obtained for the *pongamia pinnata* oil by [5]. The decrease in the yield of biodiesel may be due to formation of emulsion, increased viscosity and leading to gum formation. The NaOH concentration of 0.4% gave the maximum yield of 89%.

Effect of methanol: oil ratio on biodiesel yield

The methanol to oil molar ratio is one of the most important variables affecting the ester yields. In the present study, the methanol to oil molar ratio was varied from 4:1 to 8:1. Fig.3. shows the effect of methanol to oil molar ratio on yield of biodiesel. It was observed that the yield of biodiesel increased with increase in molar ratio at certain limit. This result is comparable with the already reported values [5, 11, 7]. At higher molar ratio, more triglyceride would have reacted.

However, an excess of methanol interferes with separation of glycerine because there is an increase in solubility. When glycerin remains in solution, it helps drive the equilibrium back to the reverse direction, lowering the yield of esters. The percentage increase in biodiesel yield decreased with increase in the molar ratio as shown in the figure.

Effect of reaction time on biodiesel yield

Studies were carried out at different reaction time such as 40, 50, 60, 70, 80 and 90 min. The yield of biodiesel versus reaction time at different NaOH catalyst and methanol to oil molar ratio of 6:1 for a reaction temperature of 60 ± 1°C is shown in Fig.4. It was observed that biodiesel yield increased with increase in reaction time from 40 to 60 min. As the reaction time increased beyond 90 min, the biodiesel yield decreased. However, for reaction time less than 40 min, the biodiesel yield was insignificant, hence it was not considered. Optimum reaction time in order to get maximum biodiesel yield found to be 60 min.

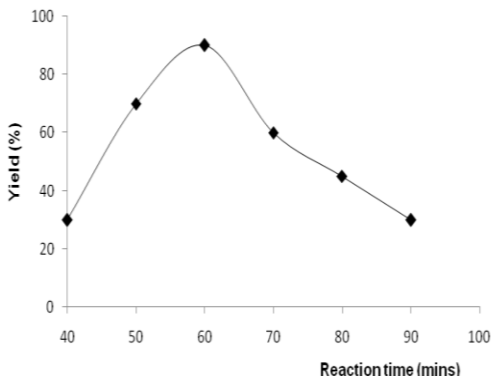


Fig 4 Effect of reaction time on biodiesel yield

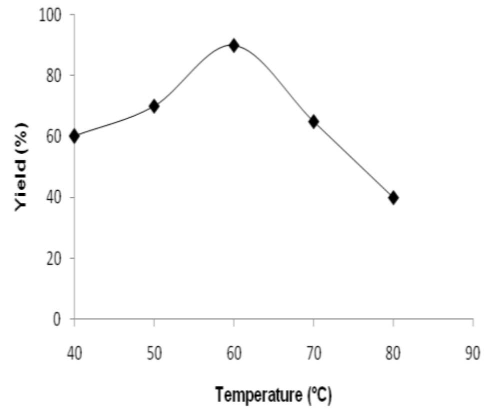


Fig 5 Effect of temperature on biodiesel yield

Effect of temperature on biodiesel yield

Catalytic transesterification of vegetable oil is normally investigated close to the boiling point of the methanol [12]. Experiments were carried out at different temperatures such as 40°C, 50°C, 60°C, 70°C and 80°C. The biodiesel yield follows an increasing trend with increase in reaction temperature up to 60 ± 1°C. This may be attributed to the fact that higher reaction temperature helps in faster settlement of glycerol. The biodiesel yield decreased beyond a reaction temperature of 60 ± 1°C. The reason may be due to saponification of the triglycerides before the completion of transesterification [5, 11, 7].

Multiple Linear regressions

Multiple regressions are defined as an extension of simple linear regression in experiments where more than one independent variable (X) is used to predict a single dependent variable (Y). The predicted value of Y is a linear transformation of the X variables such that the sum of squared deviations of the observed and predicted Y is a minimum. In our case Alkali concentration, methanol: oil ratio, time, temperature for biodiesel production are independent variable which is used to predict the dependent variable i.e. biodiesel yield. R2 value is indicated the goodness of fit of a model. In regression, the R2 coefficient is a statistical measurement of regression line fit with the observed real data points. An R2 of 1 indicates that the regression line perfectly fits the data. More generally, a nearest value of R-Squared to 1 means better prediction of one term from another (Table 1).

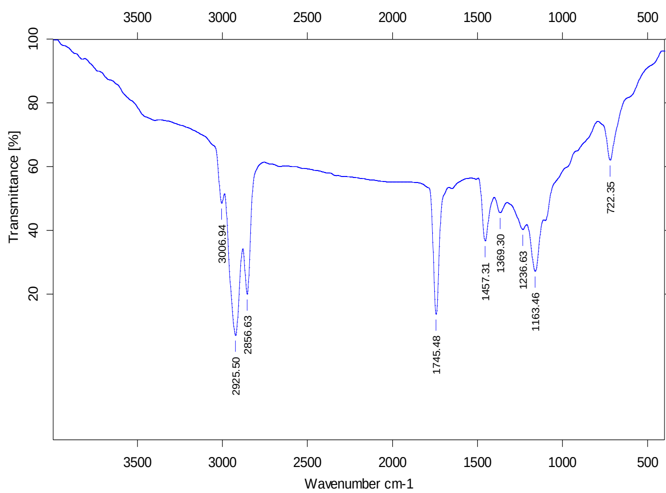
Table 1 Multiple Linear regression analysis of biodiesel yield for Figures 2, 3, 4, 5

Factors	Regression Equation	R^2 value
Alkali vs. Biodiesel Yield	$y = -214.2x^2 + 197.6x + 30.83$	$R^2 = 0.892$
Methanol: oil ratio vs. Biodiesel Yield	$y = -0.092x^2 + 5.471x - 6$	$R^2 = 0.707$
Time vs. Biodiesel Yield	$y = -0.074x^2 + 9.333x - 217.8$	$R^2 = 0.782$
Temperature vs. Biodiesel Yield	$y = -0.082x^2 + 9.407x - 187.2$	$R^2 = 0.882$

Analysis of vegetable oil and its methyl ester in FTIR

FTIR finds a feasible solution of all biodiesel components without derivation. There are many reports of FTIR applied to biodiesel analysis. FTIR is useful for quantifying the various conversions of transesterification reactions. Generally, raw oil contains a mixture of low and high molecular weight components spread over different reaction time in chromatograph with higher molecular mass being detected at higher retention time [9]. In the chromatograph the esters appear in the order of increasing number of carbon atoms and increasing unsaturation level so for the same number of carbon atoms. Numbers of peaks corresponding to saturated and unsaturated fatty acids of oil and biodiesel components were less than oils and it is due to reduction in molecular mass of individual components of the biodiesel due to transesterification process. The FTIR spectra of the prepared material are shown in Fig. 6 and 7. These demonstrate that fine variations in structure during the preparation of biodiesel. FT-IR spectroscopy is a measurement technique where by spectra are collected based on measurements of the coherence of a radioactive source using time domain or space-domain measurements of Electromagnetic radiation or other type of radiation. FT-IR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitative some components of an unknown mixture. It can apply to the analysis of solids, liquids and gases. FT-IR refers to the fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum.

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. Normally esters have vibration frequency at 1730-1750 cm^{-1}. In FTIR analysis of Mahua oil biodiesel, the peak of the band in 1743 cm^{-1}. This band conforms that ester groups are present in the biodiesel. In infrared spectrum of Mahua oil biodiesel have vibrations at 1171.88, 1364.31, 1743.52, 2856.67 cm^{-1}, and 3006.49 cm^{-1}. These values suggest this spectrum corresponds to Mahua oil biodiesel.



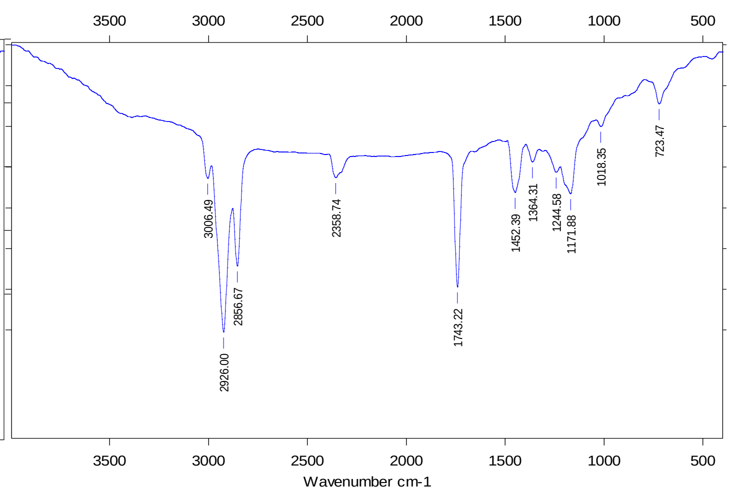


Fig 6 FTIR Spectrum for Mahua oil

Fig 7 FTIR Spectrum for biodiesel

Conclusions

Mahua is a tree with potential as an oil crop because of the high adaptability to adverse climatic and soil condition and the good quality of its oil as fuel. Biodiesel a renewable resource has become more attractive recently because of its environmental eco friendly. Biodiesel is non toxic and biodegradable. Biodiesel holds a great promise as substitute of petro-diesel in existing diesel engines without any modification. Biodiesel has been prepared by using transesterification process. The maximum conversion efficiency of 90% Mahua oil biodiesel yield can be achieved. The esterification method reduces the overall production cost of the biodiesel.

After the transesterification process, the overall viscosity of the oil is also reduced. The physico-chemical properties are analyzed for the biodiesel, and the methyl ester is analyzed using FTIR spectroscopy.

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