www.serd.ait.ac.th/reric

Parametric Study on Transesterification Process for Biodiesel Production from *Pongamia pinnata* and *Jatropha curcus* Oil

P. Mahanta*[1], J.K. Sarmah[+], P. Kalita[+], and A. Shrivastava*

Abstract – *Present work deals with the study of operating parameters on biodiesel yield in laboratory level transesterification set up. For comparison, experiments were conducted with oils of Pongamia pinnata as well as Jatropha curcus. Biodiesel fuels derived by the transesterification of these oils met the specifications of diesel fuel. Experiments were conducted to ascertain the effect of methanol, alkali catalyst, reaction time and reaction temperature on biodiesel oil yield. In case of Pongamia pinnata, maximum conversion of oil to biodiesel was 72% with 20% w/w of methanol at operating temperature of 60^0C. Conversion was 82% for Jatropha curcus oil with 25% w/w of methanol. Fuel properties of the biodiesel obtained by transesterification were tested and found to meet the ASTM specifications.*

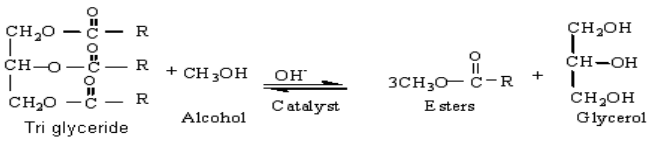
Keywords – Biodiesel, *Jatropha curcus*, *Pongamia pinnata*, transesterification, ^{1}HNMR, RPM.

1. INTRODUCTION

Biodiesel obtained from plant oil is a promising alternative fuel due to its eco-friendly nature [1], [2]. The term, biodiesel, was first introduced in the United States during 1992 by the National Soy Development Board (presently National Biodiesel Board), which has pioneered the commercialization of biodiesel in the USA [3]. Non-edible plant oils are getting importance for the production of biodiesel in recent time due to the limited availability and high demand for edible oil. Amongst the non-edible plant oils, *Pongamia pinnata* and *Jatropha curcus* are gaining importance as a source of biodiesel in developing countries. *Pongamia pinnata* is found mainly in the native Western Ghats in India, Northern Australia, Fiji and in some regions of Eastern Asia [4]. Presently *Pongamia* oil is being used by farmers in Karnataka (a southern state in India) to operate electric generators for irrigating their agricultural fields [5]. *Jatropha curcus* is a multipurpose bush/small tree belonging to the family of Euphorbiaceae, was also found to be a renewable alternative source of biodiesel.

The use of vegetable oils as an alternative renewable fuel to compete with petroleum was proposed in the beginning of the 1980 [6]. However, this oil could not be used directly in the diesel engines because of its high kinematic viscosity. High viscosity of oils would reduce the fuel atomization and increase fuel spray penetration, which would be responsible for high engine deposits [7]. One of the technologies to reduce the viscosity is by transesterification of the plant oil. Transesterification reaction can be achieved either by a base or an acid catalyst based on the acid value of plant oils. Acid value (AV) is an important indicator of vegetable oil quality. Acid value is expressed as the amount of KOH (in milligrams) necessary to neutralize free fatty acids contained in one (1) gram of oil. Acid value determination in vegetable oils is based on the acid-base titration techniques in non-aqueous solvents [8], [9]. It has been indicated by many researchers [10] that transesterified oil blended with diesel can be directly used in compression-ignition (CI) engines without any modification to the engine components.

Transesterification or alcoholysis is the chemical reaction between triglycerides and alcohol in the presence of catalyst to produce monoesters and glycerol. That is why transesterification of vegetable oils appear to be more suitable because the byproduct, glycerol has commercial value. The transesterification reaction can be represented by the following equation.



Stoichiometrically, three moles of alcohol are required for each mole of triglyceride [11], but in practice, a higher molar ratio is employed in order to displace the equilibrium for getting greater ester production. The important factors that affect the transesterification reaction are the amount of methanol and catalyst, reaction temperature and reaction time.

Commonly used short chain alcohols are methanol, ethanol, propanol and butanol. The yield of transesterification is independent of the type of alcohol used [12]. Therefore, the eventual selection of one of these three alcohols will be based on cost and performance consideration. Methanol is used commercially because of its low price. Alkaline hydroxides are the most effective transesterification catalysts as compared to acid catalysts. Potassium hydroxides and sodium hydroxides are the commonly used alkaline catalysts.

Transesterification process may be accomplished with the help of base, acid or lipase as catalyst. However,

* Department of Mechanical Engineering, Indian Institute of Technology Guwahati, Guwahati – 781039, India.

+ Center for Energy, Indian Institute of Technology Guwahati, Guwahati – 781039, India.

1 Corresponding author;
E-mail: pinak@iitg.ernet.in

base catalyzed transesterification of oils is the widely accepted method for preparing biodiesel particularly for low acid number oils. The kinetic studies of transesterification of crude and refined vegetable oils [13], *Jatropha* oil [14], *Brassica carinata* oil [15] have been reported.

In the present investigation, a batch type transesterifaction set up was developed. Two different types of non-edible plant oils, viz., *Jatropha* and *Pongamia pinnata* were taken for transesterification. Effect of amount of methanol, amount of catalyst, reaction time and reaction temperature for maximum production of biodiesel during transesterification were studied. Biodiesel samples obtained from the experiments were tested for calorific value, flash point, kinematic viscosity and cetane index as per ASTM D93, D445 and D613. It was found that the biodiesel obtained from both the species confirm to the standard specified by ASTM and comparable to diesel fuel.

2. MATERIALS AND METHODS

Experimental Set-up

The batch type laboratory transesterification set-up developed in the laboratory is shown in Figure 1 [16]. It consists of a reaction chamber submerged in a hot water bath. The reaction chamber is a portable cylindrical vessel made of stainless steel with a capacity of 1.5 liters. The lid of the vessel is removable to enable loading and unloading of reactants and products. A vertical electric motor-stirrer system is placed through the center of the lid to the reaction chamber. The electric motor is connected to the raw power through a variac to vary the speed of the mechanical stirrer. The RPM of the stirrer was measured with the help of a non-contact type tachometer. Provision for feeding the predetermined quantity of alcohol and catalyst is available through the lid of the reaction chamber as shown in the Figure 1. Temperature of the reactor was maintained at 60^0C with the help of thermostat-heater coil assembly. The temperature of water in the bath was maintained at 65-70^0C. The water bath is insulated with ceramic wool to reduce the heat loss.

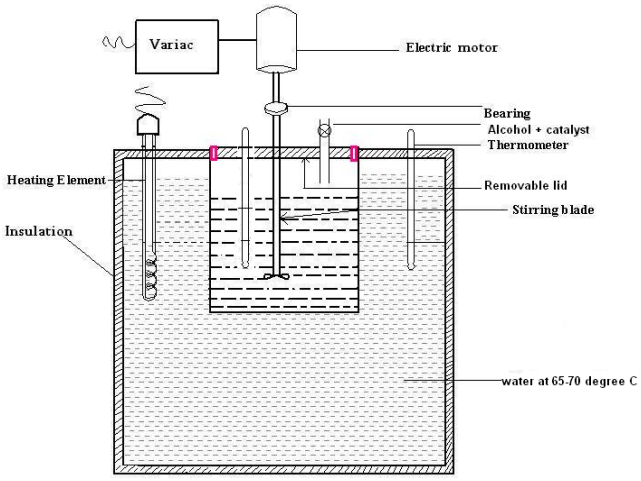


Fig. 1. Schematic diagram of transesterification set-up

Procedure

The heater in the water bath was switched on and continued heating till the water temperature attains 65-70^oC. Meanwhile, a known amount of plant oil was preheated to remove moisture in a separate container and then transferred to the reaction chamber (Figure 1). Based on the acid value of the test oil, calculated quantity of sodium hydroxide was mixed separately with methanol in a heatproof container with a narrow neck to prevent splashing. It takes about 10 to 15 minutes for complete mixing. The sodium methoxide solution was then fed through the port to the reaction vessel. The electric motor was switched on and the speed of the stirrer was maintained at 350-400 RPM.

During transesterification process, the top of the reaction vessel was kept closed to avoid heat loss. The temperature inside the reaction vessel was maintained at 60^0C with the help of the thermostat. The process was continued until a clear separation between the oil and glycerol layer was observed. Once the reaction was completed, the reaction vessel containing the mixture was then removed from the water bath and kept in standing position for 7 to 8 hours for complete separation of the two layers. Glycerol gets settled at the bottom of the container and the upper layer is a mixture of biodiesel and some amount of catalyst, soap and other impurities and collected by draining down the side of the container. To remove soap, catalyst and other impurities, biodiesel was washed three to four times with warm distilled water. For each step of washing, water taken was 25% by volume of impure methyl ester. The impure ester was taken in a separating funnel (Figure 2) to which warm distilled water was then added. Water solubilized the soap, catalyst and other impurities in the oil and settled at the bottom of the funnel, which was eventually drained out. After each wash, the pH of the water was checked. The washing was continued until the pH of the separated water reaches the range of 7-8. The final product obtained is biodiesel. *Jatropha* biodiesel is golden in color and *Pongamia pinnata* biodiesel is amber yellow.

Fig. 2. Separating funnel showing biodiesel-glycerol separation

Four experiments were conducted to investigate the biodiesel yield by fixing the variables viz., amount of methanol, amount of catalyst, reaction time, and reaction temperature. Proportions of methanol content was varied in a step of 5% w/w from 10-25% w/w. Similarly, catalyst concentration was varied at 0.5, 1.0 and 1.5% w/w, reaction time at 30 min, 60 min, 90 min and 120 min and reaction temperature at 30, 45 and 60^0C. Finally, biodiesel yield quantities of both *Jatropha* curcus and *Pongamia pinnata* were compared. The experiments were repeated thrice to validate the results.

3. RESULTS AND DISCUSSION

For maximum production of biodiesel from vegetable oils optimization of process variables is a necessity. Experiments were performed to study the effect of variation in process variables on the yield of biodiesel. In every experiment one of the reaction parameter was varied maintaining the other parameters at certain fixed value. Four parameters namely amount of methanol, catalyst, reaction time and reaction temperature were considered as subject of interest. It was found experimentally that the optimum conditions for effective biodiesel production of *Pongamia pinnata* oil is 20% w/w methanol, 1% w/w NaOH, 120 min and 60^0C and for Jatropha oil it is 25% w/w methanol, 1% w/w NaOH, 120 minutes and 60^0C.

Effect of the Amount of Methanol on the Biodiesel Production

In Figure 3 effect of variation of methanol concentration on the yield of biodiesel for both *Pongamia* and *Jatropha* oil are shown. In this figure, four different methanol concentraions have been considered.

It is seen from the figure that for both types of oil, the yield of biodiesel increases with increase in amount of methanol and reaches a maximum at some specific values of methanol concentration. In case of *Pongamia pinnata* oil, the yield of biodiesel increases from 10% methanol to 15% and then reaches the maximum at 20% w/w methanol to oil. While in case of *Jatropha* oil the same trend is observed with the exception that maximum yield of biodiesel is achieved at 25% w/w methanol to oil as shown in figure.

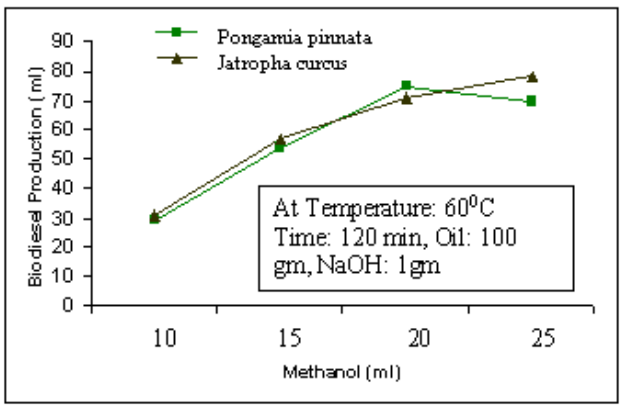


Fig. 3. Variation of biodiesel production with different amount of methanol

Effect of the Amount of Catalyst on the Biodiesel Production

Figure 4 presents the effect of NaOH concentration on the biodiesel production from *Pongamia* and *Jatropha* oil. In this figure three different amounts of NaOH, 0.5, 1 and 1.5% w/w have been considered. With 1% w/w NaOH, the biodiesel yield is 75% and 82% for *Pongamia pinnata* and *Jatropha curcus* oil respectively. It is evident from the figure that the optimum amount of catalyst required for effective transesterification is 1% w/w.

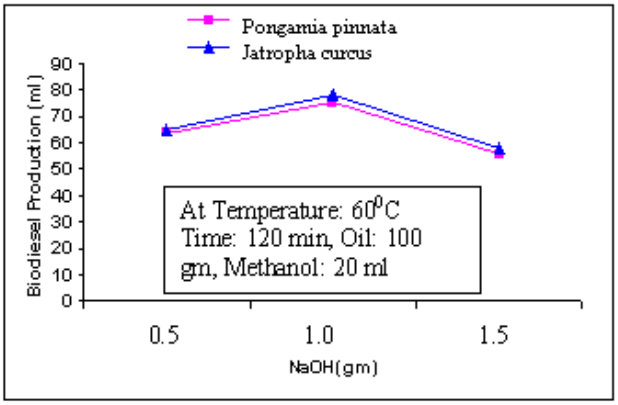


Fig. 4. Variation of biodiesel production with amount of sodium hydroxide

Effect of the Reaction Time on the Biodiesel Production

Effect of variation in reaction time on the yield of biodiesel has been studied for times (t = 30, 60, 90 and 120 minutes) and shown in Figure 5. In this figure, the lower value of biodiesel production signifies low reaction time i.e. 30 minutes and higher values signify 120 minutes of reaction time. It is evident from the figure that for both type of oils, the highest yield of biodiesel is achievable at 120 minutes of reaction time.

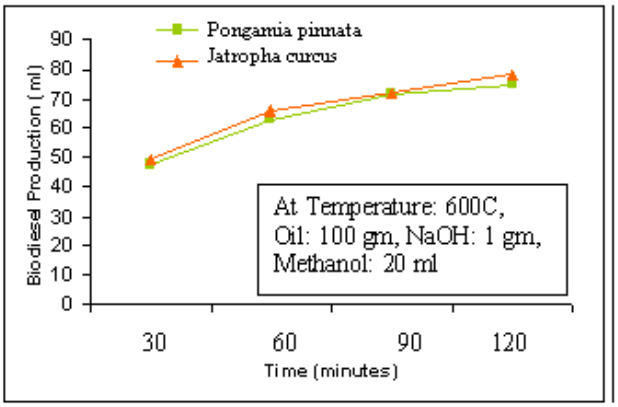


Fig. 5. Biodiesel production with time of transesterification reaction

Effect of the Reaction Temperature on the Biodiesel Production

Figure 6 presents the temperature variation effect on the yield of biodiesel. Three different temperatures; 30, 45, and 60^0C were considered. The figure indicates that at 30^0C, 50% of conversion of oil to biodiesel has been achieved. It then increases substantially and attains the

maximum at 60^0C. From the figure, it is evident that the optimum temperature for the yields of 75% *Pongamia pinnata* and 82% *Jatropha curcus* methyl esters with 1% NaOH is 60^0C. Increase in temperature beyond 60^0C was also tried but the experiments were not satisfactory due to saponification and evaporation of methyl alcohol from the reaction mixture.

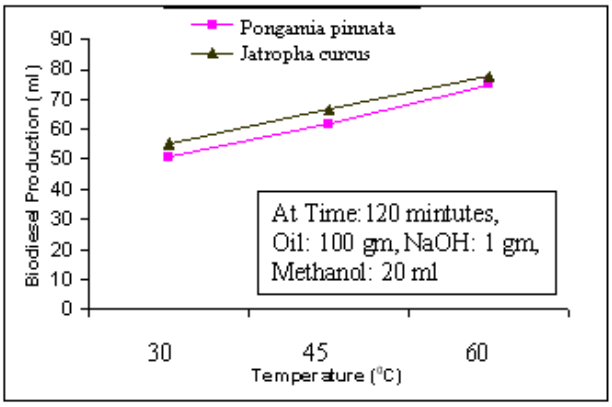
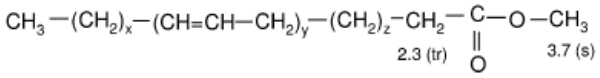


Fig. 6. Variation of biodiesel production with reaction temperature inside the transesterification reactor

Estimation of Biodiesel Conversion by ^{1}HNMR Method

Proton NMR (^{1}HNMR) is a reliable technique for estimation of biodiesel formed by the transesterification process. ^{1}HNMR spectrums of both *Jatropha curcus* and *Pongamia pinnata* methyl ester were taken. The results reveal accurate quantification of biodiesel content in the reaction mixture.

Figures 7 and 8 present typical NMR spectrum of *Jatropha curcus* and *Pongamia pinnata* methyl ester. A triplet at 2.3 ppm and a singlet at 3.7 ppm correspond to signals due to methylene protons adjacent to the ester group in triglycerides and the methoxy protons of the methyl esters.



The areas of the signals of methylene and methoxy protons (Figs. 7 and 8) have been used to calculate the yield of transesterification in a simple equation [17]:

$$C = 100 \text{ X } (2A_{ME}/3A_{CH2}) \quad (1)$$

where, C is the percentage conversion of triglycerides to corresponding methyl ester; A_{ME} is integration value of the protons of the methyl esters (the strong singlet); and A_{CH2} is the integration value of the methylene protons. The factors 2 and 3 in Equation 1 are derived from the fact that the methylene carbon possesses two protons and the alcohol (methanol derived) carbon has three attached protons. The percentage conversion obtained by this method is 82% and 72% respectively for *Jatropha curcus* and *Pongamia pinnata* methyl ester.

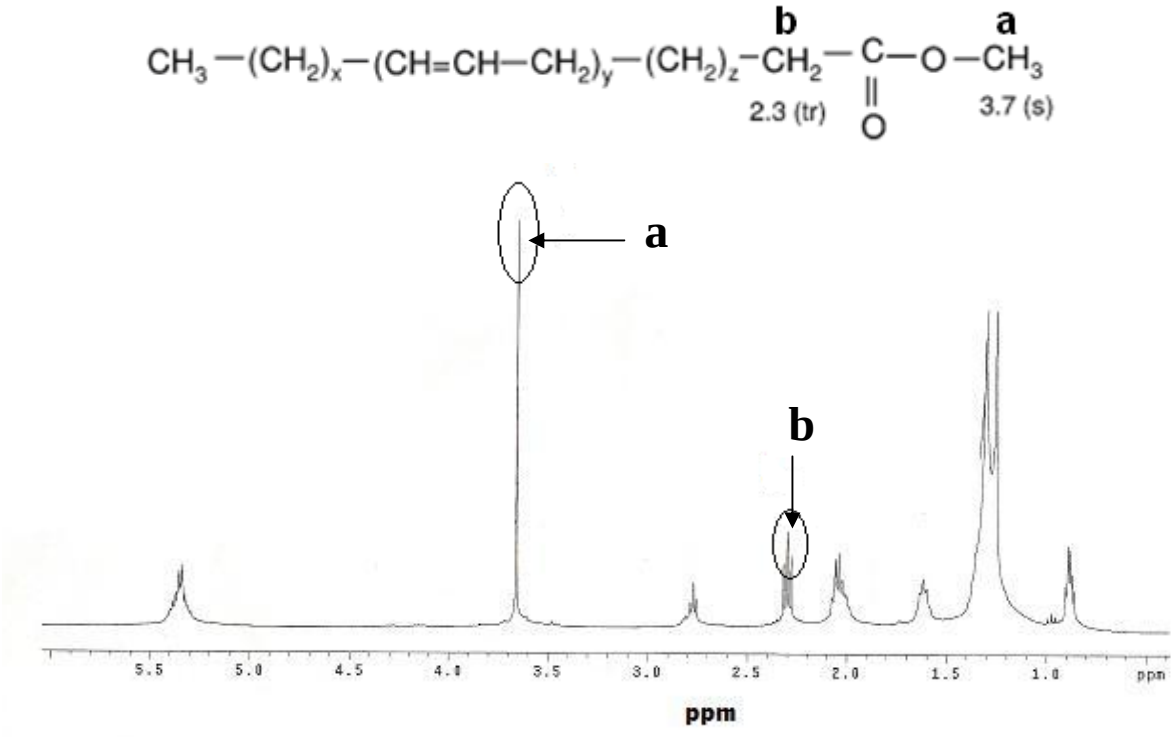


Fig. 7. ^{1}HNMR for estimation of biodiesel conversion from *Jatropha curcus* oil

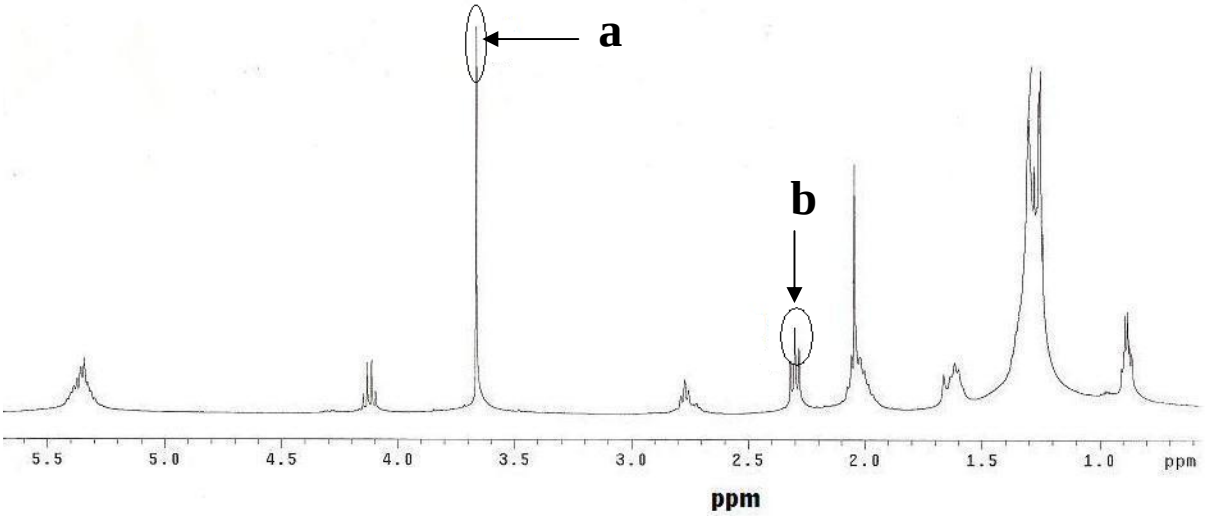


Fig. 8. [1]HNMR for estimation of biodiesel conversion from *Pongamia pinnata* oil

Properties of Raw Oil and Biodiesel from Pongamia pinnata and Jatropha curcus

The properties of biodiesel and diesel fuels are compared in Table 1. It is evident from the table that the characteristics of biodiesel are close to diesel fuels. Experiments were conducted as per ASTM methods.

From Table 1 it is evident that the kinematic viscosities of *Pongammia* and *Jatropha* biodiesel, 4.5 and 5.75 cSt, respectively, are very much close to the certified kinematic viscosity 3 cSt for diesel fuel. The flash point was also found to be higher than the petro diesel, thus it is safe for transport purpose. The specific gravity of *Jatropha* methyl ester was slightly higher than the diesel fuel but for *Pongamia* oil it was 0.850 which is similar to diesel. On the other hand, the calorific value of *Jatropha* methyl ester was found to be much closer to petro diesel than the *Pongamia* methyl ester.

The kinematic viscosities of raw oil of *Pongamia pinnata* and *Jatropha curcus* were much higher than the specified range of diesel (Table 1). Transesterification of the raw oil can effectively reduce the kinematic viscocity to the desired range. The calorific value of both the oil was found comparable to diesel fuel. The acid value, which is a dimensionless quantity was almost same for both the species of plant oil. The acid values of 1 and 1.2 for *Pongamia* and *Jatropha* oil, respectively, suggest that the base catalyzed transesterification is feasible for both types of oil species [18].

Uncertainty of the experimental set-up was evaluated and the volume uncertainty of the biodiesel yield was found to be $\pm$ 0.0254. Uncertainty of biodiesel yield was calculated based on the volume uncertainty of the oil container.

Uncertainty of the thermometer was also considered. Initially the temperature was measured with the help of copper constantan thermocouple. Also, the thermocouple was calibrated in the laboratory. Finally, the thermocouple was replaced by precision thermometer, which shows same reading of temperature as the thermocouple. Hence, the uncertainty of the thermometer for temperature was neglected.

Table 1. Physical and chemical properties of non-edible oil

Properties	Raw *Jatropha curcus* oil	Biodesel of *Jatropha* oil	Raw *Pongamia pinnata* oil	Biodiesel of *Pongamia pinnata*	Diesel
Specific gravity	0.930	0.870	0.880	0.850	0.840
Kinematic viscosity (cSt)	52.76	4.5	18.2	5.75	3
Flash point (^{0}C)	240	130	190	110	47
Calorific value (kJ/kg)	39,800	38,980	37,300	36,540	43,000
Acid value	1.2	-----	1	-----	-----

4. CONCLUSION

Physicochemical properties of *Pongamia pinnata* and *Jatropha* oils suggest that the raw oil cannot be used directly as CI engine fuel. Higher kinematic viscosity and density will result in low volatility and poor atomization in the combustion chamber of CI engine with incomplete combustion and carbon deposits on injector nozzles and on walls of combustion chamber. Therefore, transesterification is a necessity. To produce better quality biodiesel by catalytic transesterification method, one need to optimize reaction parameters viz., amount of alcohol, type and concentration of catalyst, reaction time and reaction temperature.

Optimum temperature for transesterification reaction temperature is found to be 60°C for the straight vegetable oil (SVO) of both *Pongamia Pinnata* and *Jatropha curcus* oil. However ratios of methyl alcohol to vegetable oil for the reactions were found to be different for both the SVO's (20 % and 25 % for *Pongamia* and *Jatropha* respectively). In both the cases catalyst

concentration i.e. NaOH concentration is found to be 1 % of oil. The optimum time for maximum biodiesel yield is found to be 120 minutes. The maximum yield of biodiesel obtained from *Pongamia pinnata* SVO is 72%, while in the case of *Jatropha* oil, 82% conversion to biodiesel was recorded at 25% methanol concentration of the test oil. The uncertainty of volume measurement was calculated and it was found to be +/- 0.0254.

Transesterification is a process that brings about a change in the molecular structure of the vegetable oil molecules, thus bringing down the kinematic viscosity of vegetable oils. The densities and kinematic viscosities of the *Jatropha* methyl ester and *Pongamia pinnata* methyl ester formed after transesterification were found to be very close to diesel fuel. The flash point of the methyl esters of both the plant oils was higher than the diesel fuel. The present analysis reveals that biodiesel from *Pongamia pinnata* and *Jatropha curcus* oil is quite suitable as an alternative to diesel fuel.

REFERENCES

[1] Tewari D.N. 2003. Report of the committee on development of BIO-FUEL. Planning commission, Government of India.

[2] Barnwal, B.K., and Sharma, M.P. 2005. Prospects of biodiesel production from vegetable oils in India. *Renewable and Sustainable Energy Reviews* 9: 363-378.

[3] Ramadhas, A.S., Jayraj, S., and Muraleedharan, C. 2004. Use of vegetable oils as I.C. engine fuels, a review. *Renewable Energy* 29: 727-742.

[4] Lakshmikanthan, V. 1978. Tree borne oil seeds. Directorate of non-edible oils and soap industry, Khadi and village industries commission, Mumbai, India: 10.

[5] Shrinivasa, U. 2001. A viable substitute for diesel in rural India. Current Science 80: 1483-1484.

[6] Bartholomew, D. 1999. Vegetable oil fuel, a review. *Energy Sources* 21: 221-31.

[7] Silvio, C.A., Belchior, C.R., Nascimento, M.V.G., Vieira, L. and Flueury, G.. 2002. Performance of a diesel generator fueled with palm oil. *Fuel* 81: 2097-2102.

[8] Firestone, D (Editor). 1996. Method Ca5a–40. Free Fatty Acids. *Official methods and recommended practices of the American Oil Chemists Society*, 4th ed., American Oil Chemists Society, Champaign, USA.

[9] ISO-660. 1983. E *Animal and Vegetable Fats and Oils.* Determination of Acid Value and Acidity, ISO, Geneva.

[10] Ayhan, D. 2008. Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. *Energy Conversion and Management* 49(1): 125-130.

[11] Muniyappa, P.R., Brammer, S.C., and Noureddiini, H. 1996. Improved conversion of plant oils and animal fats into biodiesel and co-product. *Bioresource Technology* 56: 19-24.

[12] Barnwal, B.K., and Sharma, M.P. 2005. Prospects of biodiesel production from vegetable oils in India. *Renewable and Sustainable Energy Reviews* 9: 363-378.

[13] Freedman, B., Pryde, E.H., and Mounts, T.L. 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists' Society* 61: 1638-1643.

[14] Foidl, N., Foidl, G., Sanchez, M., Mittelbach, M., and Hackel, S. 1996. Jatropha curcus L. as a source for the production of biofuel in Nicaragua. *Bioresource Technology* 58: 77-82.

[15] Cardonea, M., Mazzoncinib, M., Meninib, S., Roccoc V., Senatorea, A., Seggianid, M., and Vitolod, S.. 2003. Brassica carinata as an alternative oil crop for the production of bio-diesel in Italy: agronomic evaluation, fuel production by transesterification and characterization. *Biomass and Bioenergy* 25: 623-636.

[16] Kushwah, Y.S. 2006. Design, development and performance study of extraction and processing units for bio-diesel production. M. Tech Thesis; IIT Guwahati, India.

[17] Gelbard, G., Bres. O., Vargas, R.M., Vielfaure, F., and Schuchardt, U.F. 1995. 1H nuclear magnetic resonance determination of the yield of the transesterification of rapeseed oil with methanol. *Journal of the American Oil Chemists' Society* 72(10): 1239–41. 268.

[18] Ramadhas, A.S., Jayraj, S., and Muraleedharan, C. 2005. Biodiesel production from high FFA rubber seed oil. *Fuel* 84: 335-340.