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Journal of Chemical and Pharmaceutical Research

J. Chem. Pharm. Res., 2010, 2(5):599-608

ISSN No: 0975-7384
CODEN(USA): JCPRC5

Optimization of esterification and transesterification of Mahua (*Madhuca Indica*) oil for production of biodiesel

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ABSTRACT

In the present work, bio diesel was produced from Mahua (Madhuca Indica) oil through esterification followed by transesterification . Kinetic studies to optimize the preparation of Mahua Oil Methyl Ester (MOME) were carried out varying different parameters like methanol / oil molar ratio, % of excess alcohol, reaction time, temperature and concentration of acid catalyst. The results show that 4% H_2SO_4, 0.33% v/v alcohol/oil ratio, 1 hr reaction time and 65^0C temperature are the optimum conditions for esterification. Optimum conditions for the production of biodiesel from Mahua oil are 8% Sodium Methoxide , 0.33%v/v alcohol/oil ratio, 1 hr reaction time , 65 ^0C temperature and 150% v/v excess alcohol . The various fuel properties of MOME were compared with ASTM and DIN standards. The fuel properties were found to be comparable with that of diesel fuel. Mahua tree is found in abundance in most parts of India and from its chemical composition it is found that the oil is almost similar to that of other non-edible oils. It is concluded that the Mahua oil is also a potential raw material for biodiesel. The Biodiesel (MOME) produced from mahua oil is cost effective and can be a viable alternative fuel in near future.

Keywords: Mahua oil, Esterification and transesterification, Biodiesel.

INTRODUCTION

Due to recent energy crisis and dwindling reserves of crude oil the demand for alternate liquid fuels particularly the diesel is increasing. Biofuels are being given serious consideration as potential sources of energy in the future, particularly in developing countries like India. The use of edible oil to produce biodiesel in India is not feasible in view of big gap in demand and supply of such oil. As India is deficient in edible oils, some developmental works have been carried out by government of India for producing bio diesel from non traditional oil like Jatropha, karanja , neem, undi, sal, etc. Bio diesel from mahua seed is important because most of the states of India are tribal where it is found abundantly. Mahua seed contain 30-40 percent fatty oil called mahua oil[1-5]. The mahua tree starts bearing seeds from seventh year of planting. Mahua seed oil is a common ingredient of hydrogenated fat in India. It is obtained from the seed kernels and is a pale yellow, semi-solid fat at room temperature. It is also used in the manufacture of various products such as soap and glycerine [4] . Crude mahua oil generally contains high % Free Fatty Acid (FFA) and conversion of FFA to biodiesel is very important [2-4]. Properties of biodiesel depend on the nature of the vegetable oil used for preparation of biodiesel by esterification and/or trans-esterification. From the chemical composition it is found that Mahua oil is almost similar to that of other non-edible oils [5]. It is the prime reason behind selecting Mahua oil as the raw material for biodiesel production .Four well-known processes are used to reduce the viscosity, namely, dilution, pyrolysis, micro-emulsion and transesterification. Transesterification however is the current method of choice for study, which results in a fuel similar to diesel. Transesterification is a reaction between a triglyceride and alcohol in the presence of alkali catalyst to produce glycerol and ester. The molecular weight of ester molecule is one-third of oil and of low viscosity. However, higher ratio of alcohol to oil is generally employed to obtain biodiesel of low viscosity and high conversion [6]. Alkali-catalyzed transesterification is very fast compared to acid catalyzed [7-8]. Methanol or ethanol is widely used in the transesterification [9]. In this study, Mahua oil methyl ester (MOME) was prepared by using alkali catalyst as sodium methoxide by transesterification process. Trans-esterification conversion is complicated if oil contains higher amounts of FFA (>1% w/w) in which case it will form soap with alkaline catalyst. The soap can prevent separation of the biodiesel from the glycerin fraction. Crude mahua oil contains about 30% FFA, which is far beyond the 1% level. The reduction of FFA <1% is best if esterification followed by Trans-esterification. In the transesterification reaction excess of methanol is used to cause fast reaction and high degree of conversion [10]. The transesterification requires an alkali catalyst such as NaOH, or KOH which are preferred due to their low cost and large availability. Although the ester is the major product, desired recovery of glycerol is important because of its industrial uses [11-12]. In this study, Mahua oil methyl ester (MOME) was prepared by using alkali catalyst as sodium methoxide [13-14]. The problem with processing these low cost oils and fats is that they often contain large amounts of free fatty acids that cannot be converted to biodiesel using alkaline catalyst. Therefore, two-step esterification process is required for these feedstocks [15]. Initially the FFA of these can be converted to fatty acid methyl esters by an acid catalyzed pretreatment and in the second step transesterification is completed by using alkaline catalyst to complete the reaction. If the oil has high free fatty acid content and more water, acid catalyzed transesterification is suitable [16]. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol [17]. Reaction time is the controlling factor in determining the yield of methyl esters [18]. It has been observed that during the transesterification reaction, the reactants initially form a two-phase liquid system. The mixing effect has been found to play a significant role in the slow rate of the reaction. As phase separation ceases, mixing becomes insignificant. The effect of mixing on the kinetics of the transesterification process forms the basis for process scale-up and design [19]. In this present work experimental investigations have been carried out to find out the different properties of Mahua oil. Bio-diesel (Mahua Oil Methyl Ester) prepared from Mahua oil through transesterification process. Different properties of the mahua oil and its methyl ester are determined. Kinetic studies to optimize the preparation of Mahua Oil Methyl Ester (MOME) were carried out varying the different parameters like methanol / oil molar ratio, % of excess alcohol, reaction time, temperature and concentration of acid catalyst.

EXPERIMENTAL SECTION

The experimental set up is given in Figure -1.The reactor used for experiments was a 1000 ml three-necked round-bottomed flask. One of the three necks was equipped with a condenser and the other two were used for thermo-well and for sample collection respectively. A thermometer was placed in the thermo-well for temperature measurement inside the reactor. The central neck was adapted to a paddle blade impeller with a glass stirrer. The stirrer rod was passing through the neck using Teflon cap. The motor was connected to a speed regulator for adjusting and controlling the stirrer speed.

2.1. Esterification

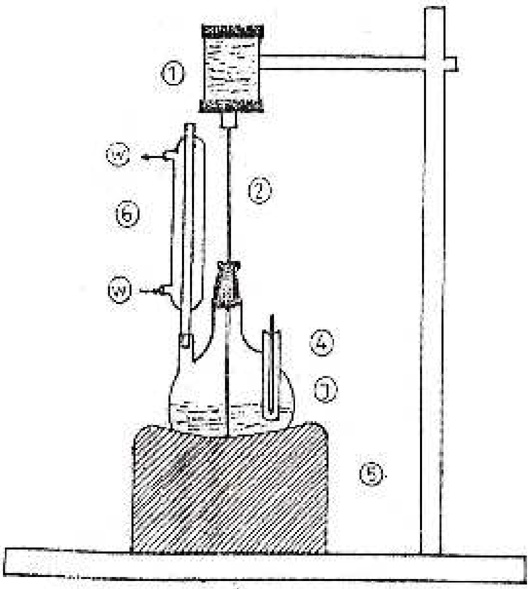
500 ml. of Mahua Oil free from water and contaminants was taken in the three-necked round-bottomed flask. Heat was supplied to the setup. Measured amount of sulphuric acid and Methanol were added to the oil .Heat was supplied and stirred continuously maintaining a steady temperature. Reaction time was conducted for 1.5 hours. Intermittently samples were collected at regular intervals and acid value was determined. After the confirmation of complete reduction of acid value to 0.1-0.5, the heating was stopped and the products were cooled. The remaining product was analyzed for acid value and it was found that the acid value varied from 0.1 to 0.5. This oil sample was further treated for transesterification step to obtain methyl esters.

2.2. Transesterification

A known amount of oil was charged to a three necked round bottom flask. Solution of known amount of catalyst sodium methoxide was prepared in methanol. The solution and the rest required amount of methanol was added to the oil sample. After proper closing of the flask it was put on mantle heater. The system was maintained airtight to prevent the loss of alcohol. The reaction mix was maintained at temperature just above the boiling point of the alcohol i.e. around 70°C to speed up the reaction. Recommended reaction times varied from 1 to 2 hours. Excess alcohol was normally used to ensure total conversion of the oil to its esters. The formation of methyl ester is checked by using thin layer chromatography (TLC) technique. Coated silica gel glass plates are spotted with Mahua oil and the product sample. The spotted samples are developed in solvent system in glass chamber using solvent. The completion of Transesterification is found by spraying the developed plate with iodine. This procedure is followed for all the samples collected at regular interval of time to check the formation of methyl ester. After the confirmation of completion of methyl ester formation, the heating was stopped and the products were cooled and transferred to a separating funnel. The ester layer containing mainly methyl ester and methanol and the glycerol layer containing mainly glycerol and methanol were separated. The methyl ester was washed and dried under vacuum to remove traces of moisture.

3. Characterization

The characterization covers the physical, chemical and thermal properties of the oil and its methyl ester. These standard values of raw mahua oil and mahua oil methyl ester (Bio-diesel) are calculated and compared. Flash point, Fire point, Viscosity, Cetane number**,** Acid value, Iodine value**,** Saponification number (SN),Calorific value etc of mahua oil and mahua oil methyl ester are determined[20-24] .



1. Electric Motor **4. Thermo-well with thermometer**
2. Stirrer **5. Water bath**
3. Three-necked Round Bottom Flask **6.Condenser**

Figure – 1: Experimental setup for preparation of methyl esters from Mahua oil.

RESULT AND DISCUSSION

Study was carried out with important process variables for optimization of esterification and transesterification reaction to achieve maximum bio diesel production. The important process variables for esterification such as concentration of acid catalyst, alcohol/oil ratio, reaction time, temperature, and % of excess alcohol; and for transesterification; concentration of alkali catalyst, alcohol/oil ratio, reaction time, temperature, % of excess alcohol are optimized.

4.1. Esterification

Esterification result shows that the concentration of acid catalyst is 4 % (H_2SO_4), alcohol/oil ratio = 0.33%v/v, reaction time = 1 hr , temperature = 65^0C for maximum esterification. It is found that the effect of temperature on acid value is an important factor for esterification reaction**.** Acid catalyst is a better choice for esterification reaction because the reduction of Free Fatty Acid is very fast and requires less time. (Fig 2-5)

Fig 2: Effect of temperature (^{0} C) on esterified oil (ml) for constant methanol/oil ratio 0.33% v/v, acid catalyst = 4%(H_2SO_4) and reaction time = 1 hr.

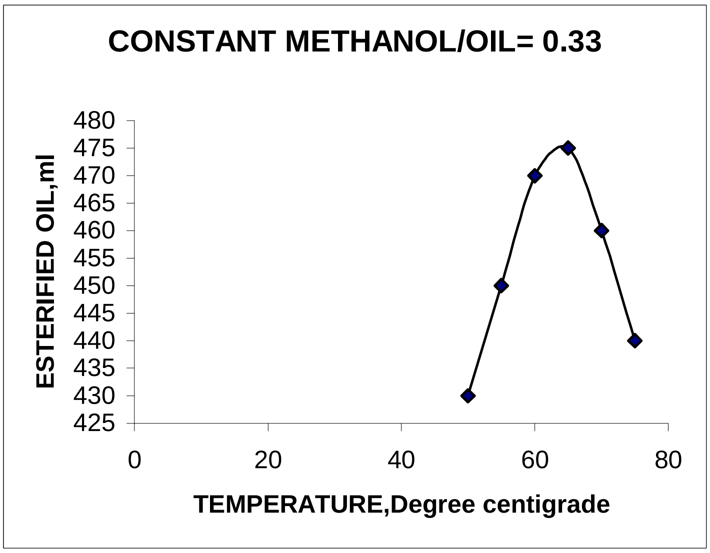


Fig 3 : Effect of % of acid catalyst and esterified oil (ml) for constant methanol/oil ratio 0.33% v/v, temperature (65^{0}C) and reaction time = 1 hr

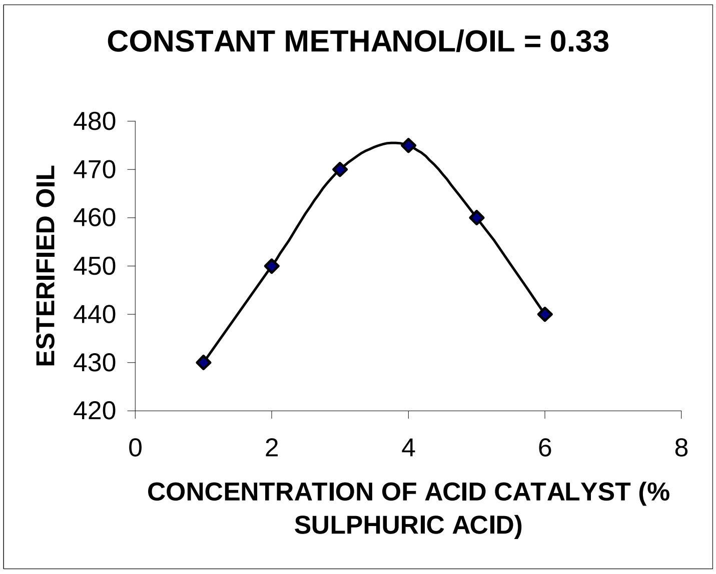


Fig 4: Effect of reaction time (hr) on esterified oil (ml) for constant methanol/oil ratio 0.33% v/v temperature (65^{0}C) and acid catalyst = 4%(H_2SO_4).

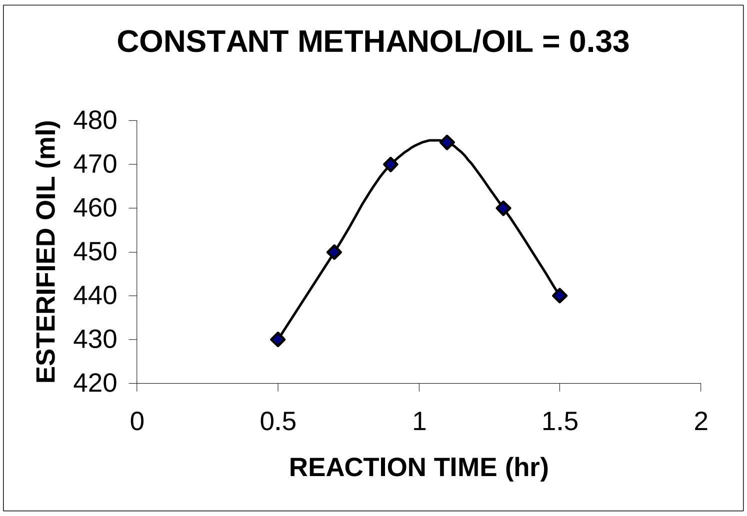
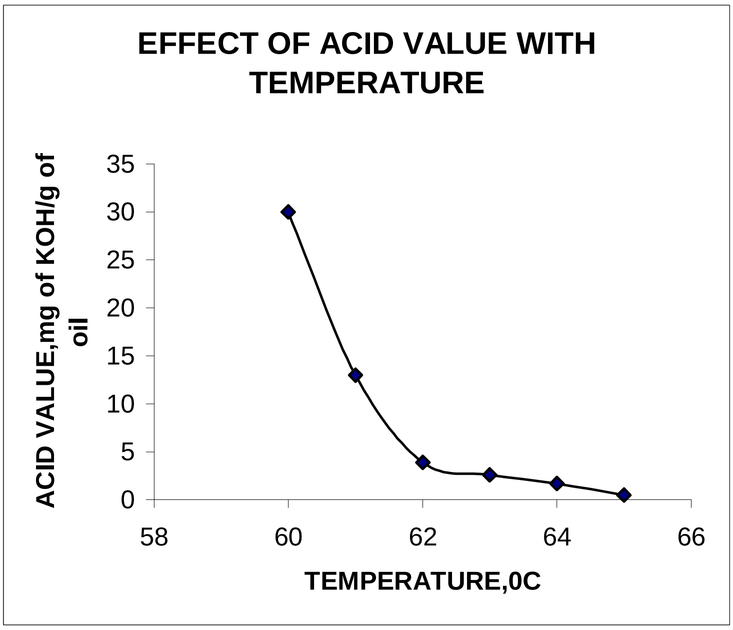


Fig 5: Effect of Temperature on Acid value for constant methanol/oil ratio 0.33% v/v ,Reaction time = 1 hr and acid catalyst = 4%(H_2SO_4)



4.2. Transesterification

For maximum bio diesel production the transesterfication reaction shows that the concentration of alkali catalyst is 8 % Sodium Methoxide, alcohol/oil ratio = 0.33%v/v, reaction time = 1 hr , temperature = 65^{0}C and excess alcohol = 150%v/v. For tranesterification alkali catalyst is a better choice because the reaction is very fast and requires less amount of catalyst. (Fig 6-9)

Fig 6: Effect of methanol/oil ratio on MOME yield for constant temperature (65^{0}C) Reaction time = 1 hr and alkali catalyst = 0.8 wt % sodium methoxide, excess alcohol = 150 %

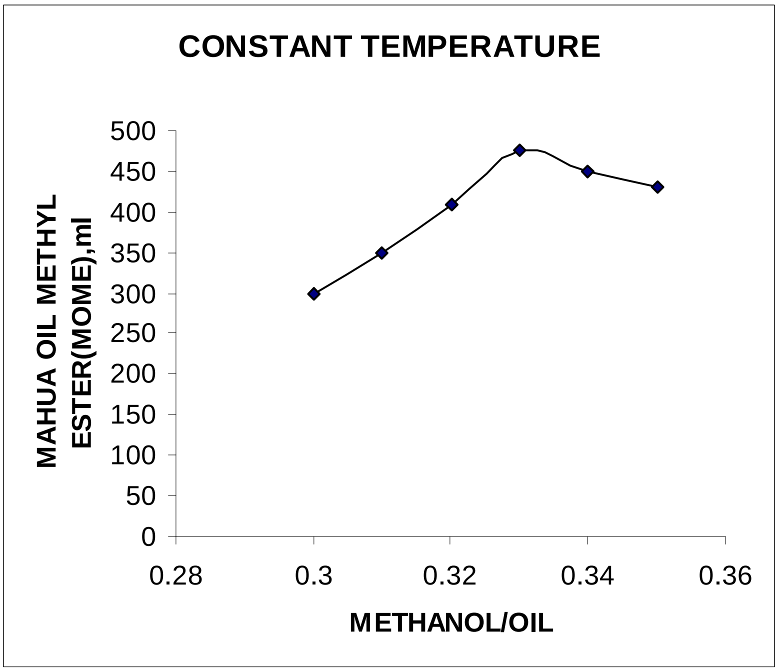


Fig 7: Effect of reaction time on MOME yield for constant temperature (65^{0}C) methanol/oil ratio 0.33% v/v , alkali catalyst = 0.8 wt % sodium methoxide, excess alcohol = 150 %

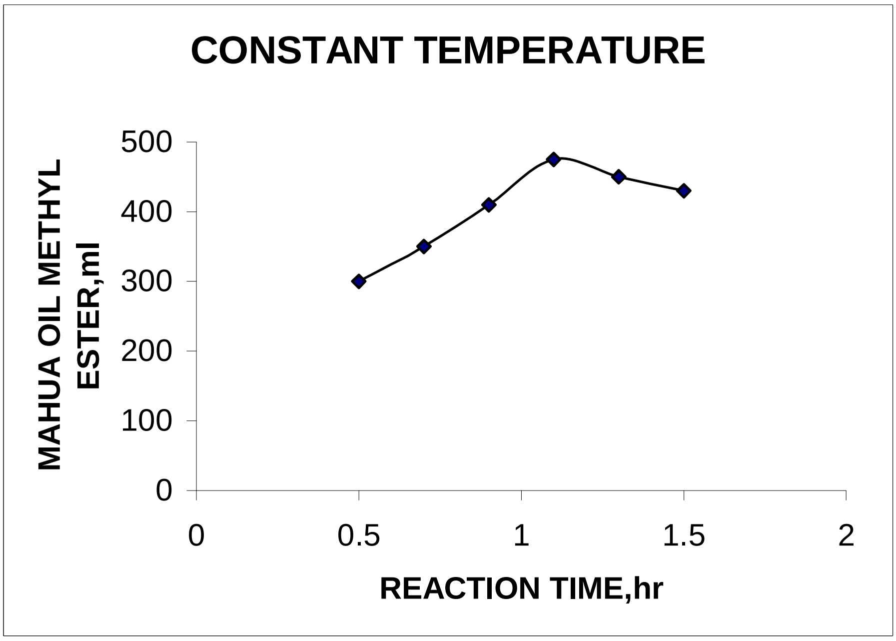


Fig 8: Effect of % of excess alcohol on MOME yield for constant temperature (65^{0}C) methanol/oil ratio 0.33% v/v , alkali catalyst = 0.8 wt % sodium methoxide, and reaction time = 1 hr.

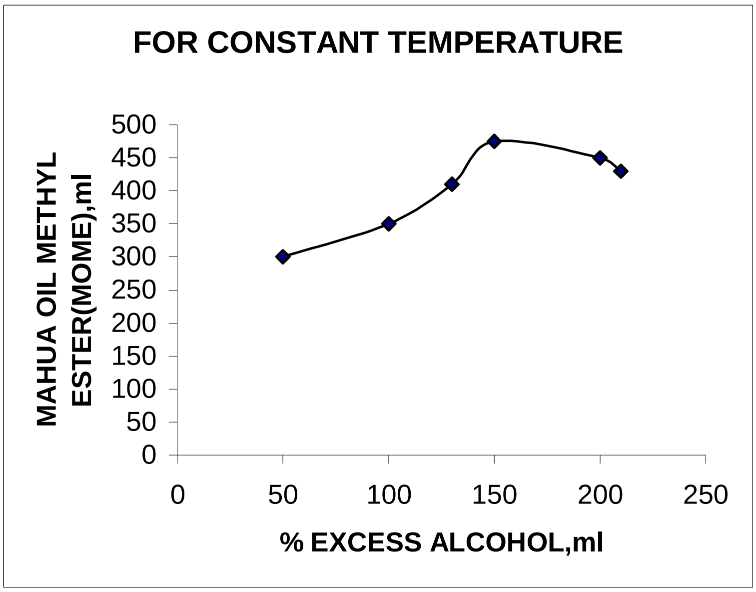
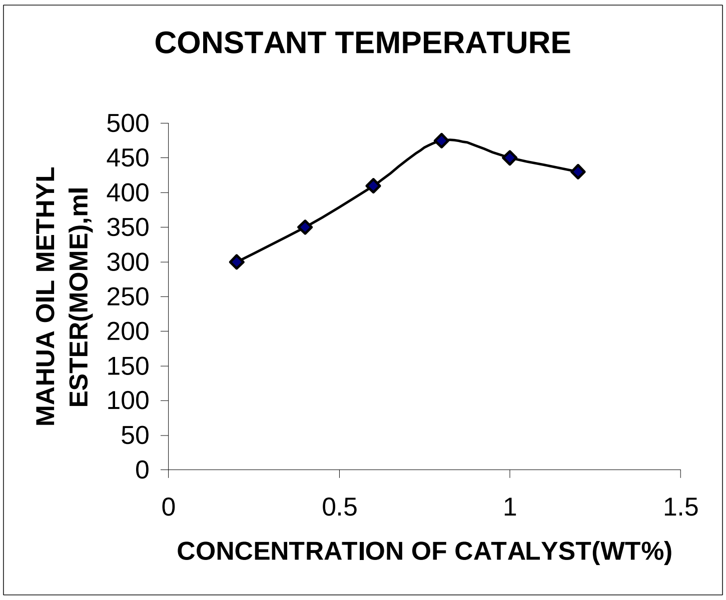


Fig 9: Effect of concentration of alkali catalyst and MOME for constant temperature (65^{0}C) methanol/oil ratio 0.33% v/v , excess alcohol = 150 % and Reaction time = 1 hr



4.3. Characterization of Mahua oil and Mahua oil Methyl Ester:

A comparison of fuel properties are made between mahua oil, mahua oil methyl ester and diesel. Then, the same was compared with ASTM and DIN standard in Table: 1. From the various properties of MOME it is found that MOME has calorific value 5% lower than diesel fuel. Kinematic viscosity and Cetane value are slightly higher than diesel, which is favorable for combustion. Flash point and Fire point are high, which is an advantage for fuel transportation.

Table 1 Comparison of Fuel properties of Mahua oil, Mahua oil methyl ester & diesel

Property	**Diesel oil**	**Mahua oil**	**MOME**	**ASTM D6751-02**	**DIN EN14214**
Density (15^0C), kg/m^3	835	945	872	875-900	860-900
Kinematic Viscosity, 40^0 C, mm^2/s	2.4	25	4.0	1.9-6.0	3.5-5.0
Flash point, ^{0}C	70	226	204	>130	>120
Fire point, ^{0}C	76	250	230	>65	>70
Cloud point, ^{0}C	-10 to-15	14	6	Summer = 4 Winter = -1	Summer = 6 Winter = 1
Pour point, ^{0}C	-35 to -15	15	1	----	-----
Acid value, mg of KOH/g oil	NM	30	0.5	< 0.8	<0.5
Calorific value (MJ/Kg)	43	35	41	40 Min	49 Max
Saponification value	NM	191	130	----	----
Colour	Light brown	Slight greenish yellow	Dark yellow	-----	-----
Cetane number	47	NM	50	----	----
Aniline point, ^{0}C	69	60	63	----	-----
Iodine value	NM	65	60	----	------
Diesel index	150	140	145	------	-----

FAME = Fatty Acid Methyl Ester.; NM = Not Measured ; ----- = Not available

CONCLUSION

The high Free Fatty acid (30%) of crude Mahua oil was reduced to less than 1% by using acid catalyst .The results show that optimum conditions for esterification are 4 %H_2SO_4, 0.33%v/v alcohol/oil ratio, 1 hr reaction time and temperature of 65 ^{0}C. For maximum(95%) bio diesel production the transesterification reaction shows that the concentration of alkali catalyst is 8 % Sodium Methoxide, 0.33%v/v alcohol/oil ratio , 1 hr reaction time , 65^{0}C temperature and excess alcohol 150%v/v. The comparison of fuel properties are made between mahua oil, mahua oil methyl ester and diesel. Then, the same was compared with ASTM and DIN standard and it is found that the reduction of viscosity is about 60-65%. Mahua Oil Methyl Ester has calorific value 5% lower than diesel fuel. Kinematic viscosity and Cetane value are slightly higher than diesel. This is favorable for combustion. Flash point and Fire point are high, which is an advantage for fuel transportation. The cloud point is higher than diesel, which creates some problem. The various properties of Mahua Oil Methyl Ester (MOME) are found to be comparable with that of the Diesel fuel. Properties of biodiesel depends on the nature of the vegetable oil to be used for preparation of bio diesel by esterification and/or trans-esterification. Bio diesel produced from Mahua oil can be used as an alternative fuel in near future.

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