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Characterization and Optimization of Biodiesel Production from Crude Mahua Oil by Two Stage Transesterification

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ABSTRACT : *Biodiesel production from Mahua seed was experimentally investigated in the present study. Expeller method was employed to extract mahua oil from its seed and was subjected to two stage transesterification due to the presence of more than 18% of free fatty acid content. In the primary stage, the FFA content was reduced to less than 2% by acid esterification using concentrated H_2SO_4 and methanol and followed by base catalyzed transesterification to convert the vegetable oil into biodiesel. The properties like density, viscosity, Calorific value, flash and fire point were analyzed and compared with other prominent biodiesel. GC/MS and FT-IR analysis were also studied to identify and confirm the presence of fatty acid methyl esters. The yield of mahua oil biodiesel was compared with reaction time and molar ratio at various temperatures and 65^oC was found to optimum for the production of biodiesel.*

KEYWORDS : *Transesterification, biodiesel, molar ratio, free fatty acid, viscosity*

I. INTRODUCTION

Petroleum diesel fuels have been found to have a very important role in the world economy. Nowadays vegetable oils show potential replacement for petro diesel due to the absence of sulphur content and friendly storage. The viscosity of Trans-esterified vegetable oil blends was found to be very close with petroleum diesel with enhanced lubricating properties. The biodegradability, non-toxicity and renewability make the vegetable oil biodiesel more suitable to be used with diesel in Internal Combustion engines. The usage of vegetable oil also helps in higher international exchanges and also contributes to carbon di-oxide sequestration and thereby helps in green house effect [1, 2]. Vegetable oil on comparison with conventional fossil fuel emits lesser quantity of unburned hydrocarbons, Particulates and Oxides of nitrogen and carbon.

The Production of biodiesel with high fatty acid contents was carried out by two step pretreatment process in which Sulphuric acid was used as a primary catalyst. In the second step methanol and Potassium hydroxide were used to produce Mahua oil biodiesel at 60°C. The comparisons of molar ratio to methanol, amount of catalyst and reaction temperature were investigated to produce palm oil biodiesel at 95°C for nine hours. It was found that the addition of Butanol enhanced the biodiesel production up to 90% with higher cetane number [4] .The rubber seed oil was found to be a promising alternative to petroleum diesel. The FFA content of rubber seed oil was found to be very much higher which was reduced to less than 2% in two step acid alkaline catalyzed transesterification process which ultimately produced fatty acid methyl esters and glycerol at the end of the reaction. The calorific value of rubber seed oil was found to be 14% less than petroleum diesel with similar other physio-chemical properties with diesel [14]. The two stage acid esterification and base esterification was carried out to produce biodiesel from Jatropa curcas L oil. Since the FFA content was more than 16%,the biodiesel yield was only less than 50% with lesser stability.$H_2SO_4$was treated as a catalyst at 60°C for 1 hour which reduced the FFA content to less than 2% and a highly stable Jatropha biodiesel was obtained at an yield of 96% [18]. The Mahua seed is found enormously in India especially in tribal and forest regions. The kernels of Mahua seed were estimated to produce nearly 35 to 45 % of oil depending upon the growth and geographical factors which is highly viscous at room temperature.

To reduce the viscosity, various methods can be employed namely heating, thermal cracking, pyrolysis, dilution and Transesterification [16]. Generally Mahua oil biodiesel was obtained by employing two stage transesterification with Acid/base catalyst, biocatalyst and supercritical Methanolysis process. The two stage trans-esterification process comprises of primarily Acid esterification to reduce the Free Fatty Acid contents and base catalyzed esterification to convert the vegetable oil into Fatty Acid Methyl ester [15-17]. In the present study, mahua seed was used to extract mahua oil by expeller process. A two step trans-esterification process was employed comprising of acid catalyzed esterification and base catalyzed esterification to convert mahua oil with higher FFA content into its corresponding biodiesel. During the transesterification reaction, Sodium hydroxide and methanol were mixed to form sodium methoxide for the production of Mahua Oil Methyl Esters. The fatty acid methyl esters were subjected to Gas chromatography/Mass Spectrometry analysis and Fourier Transform Infrared technique to identify the various FAMEs present in it. The physio chemical properties of mahua oil biodiesel was also analyzed and found within ASTM standards. An optimization study was also conducted by varying parameters like Molar ratio, reaction time, Reaction temperature and quantity of Methanol and Sodium hydroxide.

Nomenclature and Abbreviations	
GC/MS	Gas chromatography/ Mass spectrometry
FT-IR	Fourier Transform Infrared Spectroscopy
FFA	Free Fatty acid
FAME	Fatty Acid Methyl Ester
ASTM	American Society of Testing Materials
NIST	National Institute of Standards and Testing
v\v	Volume to volume ratio
w/w	Weight to weight ratio
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
CO	Carbon monoxide
OH	Hydroxide
MJ	Mega joule
H_2SO_4	Sulphuric acid

II. MATERIALS AND METHODS

The Mahua seeds were collected from Thanjavur district of Tamil Nadu and maintained with less than 6% of moisture. Expeller process was used to extract mahua oil at the quantity of 350 ml per kg of mahua seed. It was found that the free fatty acid content was about 18% by titration method. The properties of raw Mahua oil and Mahua biodiesel were determined and can be seen in Table 1 and 2 and the pictorial view of raw Mahua oil extracted and Mahua biodiesel can be seen in Fig (2). A two stage esterification process was employed with Acid esterification followed by base catalyzed esterification. The pretreatment and Transesterification experiments were conducted in laboratory conditions which consisted of 1000 cc inverted neck flask with air tight conditions. The reaction environment was maintained between room temperature and 65°C with 5% Concentrated Sulphuric acid and 0.36 v/v methanol to oil ratio. The reactant mixture was continuously stirred at 450 rpm for about 90 minutes with an interval of 15 minutes. The acid value was continuously monitored at these intervals by titration method till the optimum value was achieved. The pretreatment process was followed by base catalyzed reaction in which a molar ratio of 1:6 (oil to methanol molar ratio) was employed.0.8% (w/w of Sodium hydroxide to oil) was used as a catalyst to treat and neutralize the fatty acids [3,13].

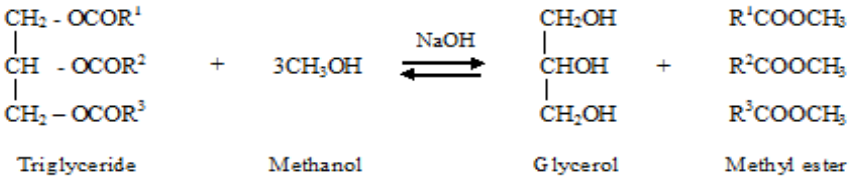

Fig 1. Transesterification reaction of Mahua oil biodiesel

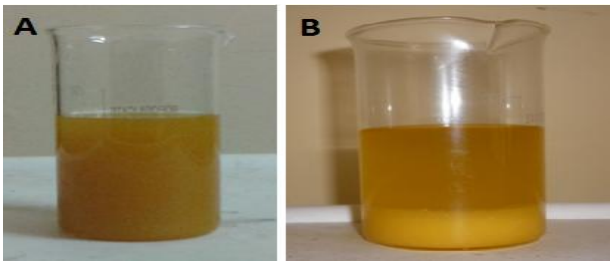

Fig 2. Comparison of Raw Mahua oil (A) with trans-esterified Mahua oil biodiesel (B)

Table 1
Comparison of Physio-Chemical Properties of Raw Mahua oil with diesel and vegetable oil

Properties	ASTM D6751	Straight Diesel [a]	Mahua Oil	Jatropha Oil [b]	Rubber seed oil [c]
Density at 15°C (Kg/m³)	860-900	839	955	912	910
Kinematic viscosity at 40°c(mm^2/s)	1.9-6.0	3.18	24.58	8.72	66.2
Calorific value (MJ/Kg)	……..	44.8	36	40	37.5
Flash point (°c)	Min 130	68	232	125	198
Carbon residue (%)	……..	0.1	3.7	…..	….
Ash content(%)	<0.02	0.01	0.9	…..	….
Acid value, mg KOH	<0.8	0.35	38	10.47	34
Cetane number	……..	51	……	57	……

[a]Sinha et al(2008),[b]Deng.X et al(2010),[c]Ramadhas et al(2005)

The reaction was carried out in a 1000cc inverted glass funnel as a separator which separates fatty acid methyl esters and glycerol as given in Scheme 1.The Transesterified Mahua biodiesel along with glycerol settlement is shown in the Fig 2. Gas chromatography and Mass spectrometry analysis was performed on the fatty acid methyl esters using JEOL GC MATE II and the FAME's were identified as given in the Table 3 and Fig 3. The Fourier Transform Infra red analysis was also performed on the sample to confirm the presence of fatty acid methyl esters as given in Fig 4. The physio chemical properties like density, viscosity, flash point, fire point, calorific value, carbon residue, ash content, acid value, cetane number were determined and found to be within ASTM standards as shown in Table 2 [6,7].

Table 2
Comparison of Physio Chemical Properties of Mahua Oil Methyl Ester with other biodiesel

Properties	ASTM D6751 Biodiesel	Straight diesel [a]	Mahua Biodiesel	Jatropha biodiesel [b]	Rubber seed oil Biodiesel [c]
Density at 15°C (Kg/m³)	860-900	839	872	880	874
Kinematic viscosity at 40°c(mm^2/s)	1.9-6.0	3.18	3.9	4.328	5.81
Calorific value (MJ/Kg)	…….	44.8	39	40	36.5
Flash point (°c)	min 130	68	205	140	130
Fire point (°c)	min 145	103	218	155	145
Carbon residue(%)	…….	0.1	0.2	0.25	0.24
Ash content(%)	<0.02	0.01	0.02	0.02	0.02
Acid value, mg KOH	<0.8	0.35	0.5	0.32	0.118
Cetane number	…….	51	52	57	54

[a]Sinha et al(2008),[b]Raheman et al(2005),[c]Ramadhas et al(2005).

Characterization of Biodiesel : Gas chromatography /Mass spectrometry analysis and Fourier Transform Infrared analysis were employed to study the Trans esterification reaction. JEOL GC MATE II data system equipped with a double focusing and high resolution impact helium gas was used as a carrier. The time range was 60 to 600 ionizations. The scan range of FTIR spectrometry was found to be MIR 450 to 4000 cm^{-1} and the resolution was 1.0cm^{-1}.The biodiesel samples were injected at a particular time intervals and its corresponding peaks for the presence of monoglycerides, triglyceride, glycerol and other methyl esters were compared with NIST library as given in Table 3 [17]. In the FT IR analysis as shown in Fig.4, a strong signal was identified in between wave numbers 1500 cm^{-1} to 2000 cm^{-1} which confirmed the presence of fatty acid methyl esters. A group of carboxylic acid compounds was found between 2855 cm^{-1} and 2926cm^{-1}.Aliphatic chloro and fluoro compounds were found between 723 cm^{-1} and 1117 cm^{-1}.The presence of alcohols with OH and CO stretch were also seen [8].

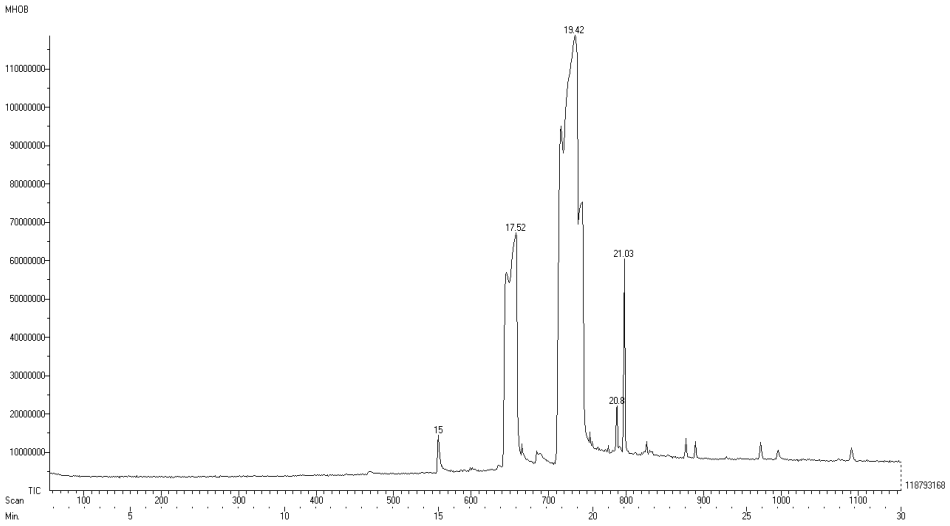

Fig 3. GC/MS Mass Spectrum of Mahua Biodiesel

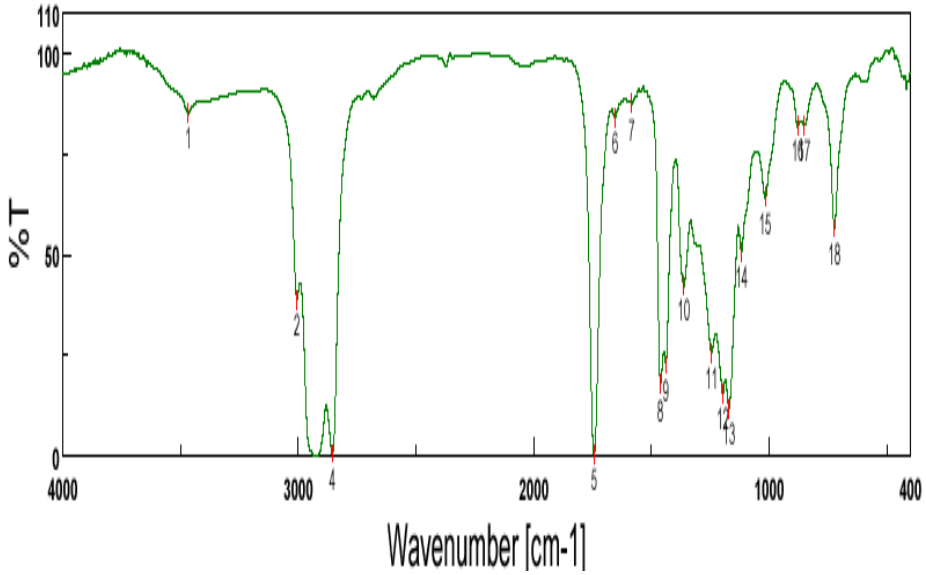

Fig 4. Fourier Transform Infrared spectrum of Mahua Biodiesel

Table 3
Composition of Fatty Acid methyl ester in Mahua biodiesel

Peak No	Retention time(min)	Description of the ester	Name of the Acid	Chemical formulae	Scan	Ions
1	15.00	Tridecanoic acid 12 methyl methyl ester	Pentadecanoic acid	$C_{15}H_{30}O_2$	558	1716
2	17.57	Pentadecanoic acid 14 methyl methyl ester	Margaric Acid	$C_{17}H_{34}O_2$	660	3262
3	19.72	10 Octadecanoic acid Methyl ester	Nonadecylic acid	$C_{19}H_{36}O_2$	746	3223
4	20.80	Methyl 9,12 epithio 9,11 octadecanoate	Palmitic acid	$C_{16}H_{32}O_2S$	789	2237
5	21.50	Mono(2,2,6,6-tetramethyl-4-piperidinyl) ester	Decanedioic acid	$C_{19}H_{24}NO_4$	799	2535

III. RESULTS AND DISCUSSION

Acid Catalyzed esterification : The Fig 5 shows the variation of FFA with reaction time at various reaction Temperatures. The Acid value of Mahua oil was initially found to be 18% (36mgKOH/g) which makes the Mahua oil unsuitable for engine operation. The raw Mahua oil was treated with 3.5% (v/v) of Concentrated H_2SO_4 and 0.35(v/v) of Methanol to oil ratio. The pretreatment reaction was carried out at room temperature, 50°C and 60°C with the above said composition of Methanol and Concentrated H_2SO_4. At room temperature the conversion efficiency was only 50% and with increase in reaction temperature, the FFA content was brought down to less than 2% as shown in the Fig 5 which may be due to formation of moisture at elevated temperatures. The Methanol to oil at 0.35(v/v) at 65°C for 90 minutes reaction was found to be optimum to reduce the free fatty acid content [5].

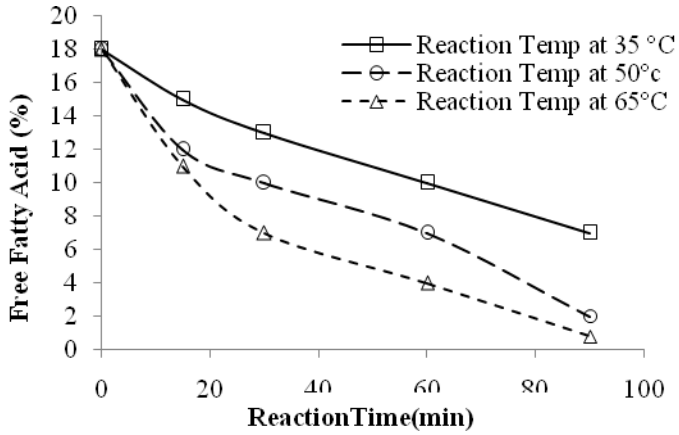

Fig 5. Effect of Reaction time on FFA reduction

Base Catalyzed Transesterification: The base catalyzed transesterification reaction was carried out at various molar ratios of 3:1,6:1 and 9:1.The reaction temperatures were maintained at 35°C,50°C and 65°C and methanol was mixed in the proportions of 0.29 (v/v) with 0.8% of Sodium hydroxide to form Sodium meth-oxide and the entire mixture was mixed with acid esterified oil. The mixture was stirred at 450 rpm using a magnetic stirrer for 2 hours to neutralize the triglycerides into fatty acid methyl esters and glycerol was obtained as by product. At 35°C the yield of biodiesel was found to be 77% for 90 minutes at molar ratio 1: 6 as shown in Fig 6 whereas at 50°C and 65°c the yield of biodiesel was found to be 82% and 89% respectively.

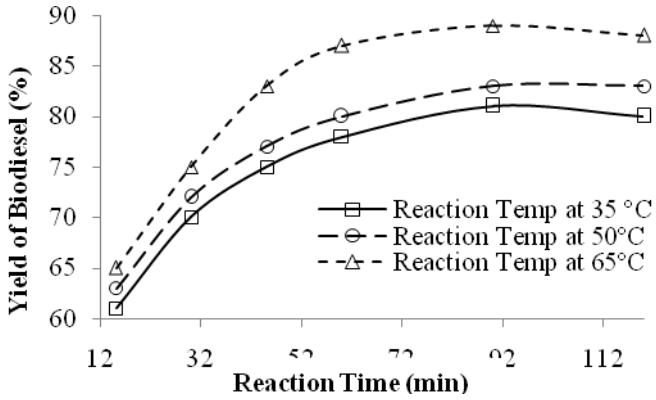

Fig 6. Effect of Reaction time on Biodiesel yield

The optimum yield of biodiesel was noticed at 65°C reaction temperature for a continuous stirring of 90 to 100 minutes as shown in Fig 6 . At higher reaction temperature (more than 65°C), the transesterification reaction was found to deteriorate which may be due to methanol evaporation [10,12] .

3.3 Effect of Methanol to oil molar ratio on Biodiesel yield

The Fig 7 shows the variation in the yield of biodiesel with molar ratios at 35°C,50°C and 65°C reaction temperatures respectively. It can be seen that at 35°C reaction temperature the conversion efficiency of oil to biodiesel was found to be 77% at molar ratio 3:1.The conversion efficiency showed a slight increase up to 82% at the molar ratio 6:1 and with further increase in molar ratio, the biodiesel yield was found to decrease gradual manner.

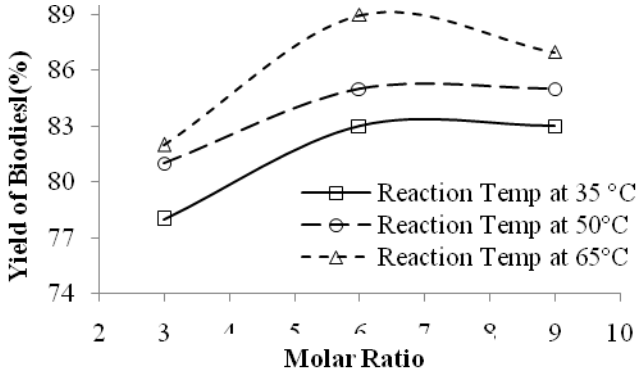

Fig 7. Effect of Methanol to oil molar ratio on Biodiesel yield

On increase in the reaction temperature to 50°C and 65°C the yield of biodiesel showed a noticeable increase up to 84% and 89% respectively at 6:1 molar ratio as shown in the Fig 7.Further increase in methanol showed no significant yield of biodiesel. The excess methanol added during the process has been removed by fractional distillation continued by washing [11].

IV. CONCLUSION

The expeller method was found to be suitable for extracting Mahua oil at 350 ml per kg of Mahua seed. Using titration technique, the free fatty acid content of mahua oil was found to be 18% which was reduced to less than 2% by acid esterification in which 5% of concentrated Sulphuric acid and methanol were added. The base catalyzed transesterification with sodium hydroxide and methanol at molar ratio of 1:6 was found to be very effective which yielded 89 % of biodiesel. The biodiesel production was optimized with reaction temperature, reaction time and molar ratio in which the reaction temperature of 65°C yield more than 85% of

mahua oil biodiesel than 35^{o}C and 50^{o}C of reaction temperature. The Mahua oil biodiesel was characterized using Gas chromatography Mass spectrometry and Fourier transform Infrared techniques in which Pentadecanoic acid, Margaric Acid, Nonadecylic acid, Palmitic acid and Decanedioic acids were found in prominent quantities.

V. ACKNOWLEDGEMENT

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