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A Two Step Catalytic Production and Characterization of Biodiesel from Non-Edible Oils (*Pongamia pinnata* and *Mahua indica*).

Raman Rao[1], Soumya Srivastava[2], and Debjani Mukherjee[2]*.

[1]Sardar Swaran Singh National Institute of Renewable Energy, Kapurthala-144601, Punjab, India
[2]School of Biotechnology and Biosciences, Lovely Professional University, Phagwara, Punjab, India – 144806

ABSTRACT

Biodiesel is gaining attention as an alternative fuel to diesel engines as it is natural, eco-friendly and alternative diesel fuel which is obtained from renewable resources like animal fats and vegetables oils. In the present study, biodiesel has been produced from non-edible oils i.e. *Pongamia pinnata* (Karanja Oil) and *Madhuca indica* (Mahua Oils) using two step catalyzed transesterification reaction (Acid method followed by Alkali method). To carry out the optimization of the transesterification process, one of the important parameters, i.e., reaction temperature was optimized and it was observed that maximum yield was obtained at 60^{o} C. Favorable results were obtained for physiochemical analysis (Density, Flash point, Fire point, Acid value, specific gravity and viscosity) of oils in context to Biodiesel standards (ASTM). Biodiesel production and characterization was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). A yield of 75% and 84.5% was obtained from pongamia pinnata and mahua oil by using two step method with a reaction mixture containing 0.5% w/w of H_2SO_4 for acid pre-treatment, 1% w/w of KOH and methanol in a ratio of 1:6 (in mole per mole).

Keywords: Karanja oil, Mahua oil, Transesterification reaction, Biodiesel, Optimization.

Corresponding author

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INTRODUCTION

Biodiesel is the mono-alkyl esters of fatty acid derived from vegetable oil or animal fat, gas demonstrated a number of promising characteristics including reduction of exhaust emission [1]**.** Biodiesel is a renewable, natural and domestic fuel made from edible and non-edible oils. It holds no petroleum, is nontoxic and biodegrable. It is an alternative fuel for diesel engines. By continuous consumption of fossil fuel or crude oil results, speedy decline in reserve of fossil fuels occurs [2]. Recently, the developing countries like India and China have experienced a significant increase in energy demand. The world largest oil producer's countries have suffered from much warfare, political and social instability. Diminishing the fossil fuel resources and coupled with the steady increase in energy consumption. It has spurred research interest in the alternative and other renewable energy sources. The growing demand for fuel and the increasing concern for the environment due to the use of petroleum products have led to the increasing popularity of biodiesel as a useful alternative and environmentally friendly energy resource. World annual petroleum consumption and vegetable oil production is about 4.018 and 0.107 billion tons [3]. Hence, the contribution of non-edible oils such as Pongamia Pinnata oil and Mahua oil will be significant as a non-edible oil source for biodiesel production. But direct use of animal fats and vegetable fats may cause some problems in engine like incomplete combustion, poor fuel automization and high lubrication oil contamination due to high viscosity. Therefore several methods are available for decreasing the viscosity of oil like blending, pyrolysis, emulsification and transesterification [4]. Out of these methods, transesterification is used widely on industrial level [5]. The oil extracted from these species especially Pongamia Pinnata and Mahua oil have environment as well as economic benefits. Biodiesel is the most attractive alternative fuel for diesel engines. It is produced from plant and animal fats. Emission from the use of biodiesel in combustion engines are greatly reduced compared to conventional petroleum diesel fuels by up to 100% sulphur dioxide, 48% carbon monoxide, 47% particulate matter, 67% total unburned hydrocarbons, and up to 90% reduction in mutagenicity [6-8].

Biodiesel also emits less pollutant than petroleum fuel. But its production has some limitations like dependency on the area and season in which the particular oil feedstock is produced and food vs. fuel problem [9]. Since most of the biodiesel is derived from edible oils like soya bean, sun flower, palm oil etc. These oils are essentially edible in India and other developing countries. Also edible oils are deficient in India. On the other hand diversion of edible oils as feed stock for biodiesel production leads to food crisis. Therefore focus is given on non-edible oils to use as feed stocks for the production of biodiesel to reduce the cost of biodiesel [10]. Biodiesel is generally produced by the transesterification (alcoholises) of vegetable oil or animal fat and alcohol to yield Fatty Acid Methyl Esters (FAME) and glycerol [11]. Methanol was commonly used for transesterification process because it is cheaper than ethanol and its recovery is also easier [12].

MATERIALS AND METHODS

The aim of present study is to achieve the maximum yield of biodiesel from the non-edible oils by using two step catalyzed transesterification method (acid method followed by alkali method). For this work, the oils, Pongamia pinnata and Madhuca indica, were purchased from Jalandhar, Punjab.

Pongamia Pinnata and Madhuca indica

Table 1: Fatty Acid Composition of Pongamia Pinnata Oil [24].

Fatty Acid	Molecular Formula	Percentage
Palmitic Acid	$C_{16}H_{32}O_2$	11.65
Stearic Acid	$C_{18}H_{36}O_2$	7.50
Oleic Acid	$C_{18}H_{34}O_2$	51.59
Linoleic Acid	$C_{18}H_{32}O_2$	16.64
Eicosanoic Acid	$C_{20}H_{40}O_2$	1.35
Dosacasnoic Acid	$C_{22}H_{44}O_2$	4.45
Tetracosanoic Acid	$C_{24}H_{48}O_2$	1.09

Due to pressure on edible oils like rape seed, ground nut, mustard and soyabean oil etc, non edible oils like Pongamis pinnata (Karanja oil) and Madhuca longifolia (Mahua oil) are considered as better source for biodiesel production. Fatty acid composition of Pongamia pinnata and Madhuca longifolia is shown in Tables 1

and 2, respectively. Pongamia pinnata and Madhuca longifolia's tree and seed shape are shown in Fig.1 and Fig.2, respectively.

Table 2: Fatty Acid Composition of Madhuca indica Oil [25].

Fatty Acid	Molecular Farmula	Percentage
Palmitic Acid	$C_{16}H_{32}O_2$	24.5
Stearic Acid	$C_{18}H_{36}O_2$	22.70
Oleic Acid	$C_{18}H_{34}O_2$	37.0
Linoleic Acid	$C_{18}H_{32}O_2$	14.3

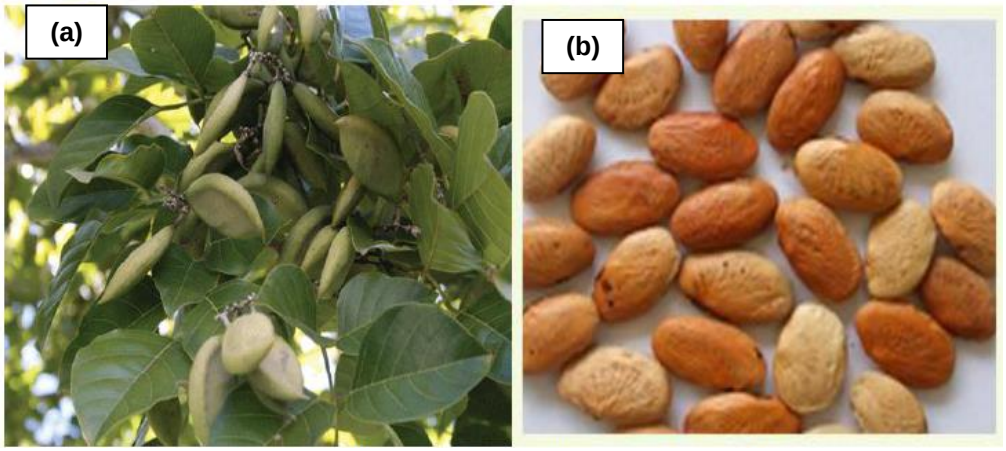

Figure 1: (a) Tree and (b) seed shape of Pongamia pinnata.

Figure 2: (a) Tree and (b) seed shape of Madhuca longifolia.

Preparation of Catalyst

For preparation of the catalyst for the transesterification reaction [13,14], 0.85gm of NaOH was added to 14.28 ml of methanol and mixed thoroughly by means of a magnetic stirrer to obtain methoxide.

Transesterification Reaction

Factors which affect the transesterification reaction are amount of methanol, sodium or potassium hydroxide, reaction time and reaction temperature. In industry generally molar ratio of 6:1 is used to obtain higher yield of methyl esters. With using high molar ratio, the yield of methyl ester increases, but its recovery becomes difficult due to the poor separation of glycerol.

Reaction temperature also influences the yield of biodiesel. Therefore the reaction is generally carried out at a temperature near to the boiling point of methanol (60°C to 70°C) at atmospheric pressure. But further increase in temperature decrease the yield of biodiesel [15].

Another parameter affecting the yield of biodiesel is the reaction time. Different researchers have used different reaction time for the transesterification reaction. The reaction mixture is generally stirred for 90 minutes followed by its transfer to separation funnel [16].

Acid Method

Based on the discussion in section 2.2, the oils are first pre-treated by acid pre-treatment method. It includes preheating of oil sample in water bath at 80°C for 30 min. Then the oils are cooled down to temperature of 60°C. Now methanol in a ratio of 1:6 (in mole per mole) and acid catalyse mixture solution (0.5% w/w of H_2SO_4) is added is to the oil and mixing is done for 2 hrs at 55°C to 60°C on magnetic stirrer at 300-400 rpm.. After the reaction is over, the mixture was kept in a separatory funnel for 8 hours. Finally it shows two distinct layers in which upper layer is of ester and lower is glycerol layer. Upper ester layer is stored for further reaction [17]. Observation of the temperature during the mixing of oil and methoxide must be continued, to maintain the constant temperature [13,14,18].

Alkali Method

The pretreated oil is taken in a reaction flask with methanol ratio of 1:6 (in mole per mole) and 1% w/w of KOH. The reaction mixing is done on magnetic stirrer at 65–70 °C for 2 hrs at 600 rpm. Finally the reaction solution is kept in a separating funnel for 8 hrs. The top layer of transesterified oil is measured and stored and pour back into the beaker [13,19,20].

Purification of Biodiesel

After the removal of glycerol, washing of biodiesel is done by using warm distilled water in the separator funnel. This washing process was repeated more than 3 to 4 times until the water becomes completely transparent. Then the biodiesel was transferred in a clean beaker. It is useful to indicate that if the pH is too high, washing process should be performed for 2 to 3 times more [13].

Drying of Biodiesel

The purified ester so formed may contain some amount of methanol and water. Therefore to remove water content and methanol, ester layer is heated in hot plate at 100°C for 15-30 mins.

Characterization of Biodiesel

The biodiesel obtained can be characterized for the following properties: pH, percentage yield, specific gravity, carbon content, acid value, saponification value, moisture content, viscosity, and density, flash and fire point. The procedure for these properties can be as per ASTM (American Standard for Testing Materials) [8,21].

RESULTS AND DISCUSSION

Optimized Process Parameter for the Production of Pongamia and Mahua Biodiesel

To optimize the process of transesterification, the parameters involved in the process are identified. The reaction was proceed at different temperature (40ºC, 50ºC, 60ºC, 70ºC, 80ºC and 90ºC) and the maximum yield of 75% and 84.50% was obtained at 60 ºC as compared to other temperature range (Table 5 and Fig.7).

Quantitative Analysis of Biodiesel yield

Percentage yield of biodiesel produced depends upon content of fatty acid methyl esters present in a particular type of seeds. It was observed that biodiesel yield of Mahua oil is 82.5% (Table 3 and Fig.4) which is

9.5% more than that of yield from Pongamia i.e. 73% (Table 3 and Fig.3). This determines that Mahua seeds contain more amounts of fatty acid methyl esters. Comparative analysis of biodiesel produced from pongamia oil and Mahua oil is shown in Fig.5.

Characterization of Fatty Acid Methyl Esters (FAME)

Physiochemical Properties

Favorable results were obtained for physiochemical analysis of oils in context to Biodiesel standards (ASTM) as shown in Table 6.

Analysis of Kinematic Viscosity

The kinematic viscosities of biodiesel were determined at 40°C (ASTM D445) as this is the temperature prescribed in biodiesel and petro-diesel standards [22]. The comparison of kinematic viscosity of pongamia and mahua biodiesel at different set of temperature is shown in Table 4 and Fig.6.

The viscosity of Pongamia biodiesel and Mahua biodiesel was obtained as 4.920 cSt and 4.0 cSt respectively at 40^{o}C. Whereas it was observed that with the increase in temperature there was decrease in kinetic viscosity of Pongamia biodiesel (Table 4 and Fig.6).

Density and Viscosity

The densities of Pongamia biodiesel and Mahua biodiesel at 40˚C are observed as 860 Kg/m^3 and 872 Kg/m^3 respectively. Whereas the kinemetic viscosity of pongamia and Mahua biodiesel is found to be 4.920 cSt and 4.0 cSt respectively at 40˚C. On increasing the temperature, value of viscosity decreases which justifies the inverse relationship between viscosity and temperature.

A high value of density and viscosity is disadvantageous as these both properties are important for the proper flow of fuel through the pipeline and also higher value of density and viscosity will increase the smoke content also.

Pour Point and Cloud Point

Cloud point and pour point are the measure of flow properties of a fuel and determine the wax contents (23). The cloud point and pour point of pongamia biodiesel was found to be 7°C and 6°C, respectively. Further, the pour point of Pongamia biodiesel and Mahua biodiesel are generally 4°C and 1°C. The high value of pour point and cloud point for pongamia biodiesel suggest that pongamia biodiesel is more suitable for storage and transportation for long time as compared to mahua biodiesel.

Fire Point and Flash Point

These two parameters are responsible for the safer handling of fuels. Higher value of flash point and fire point makes them useful in those places where the temperatures are high. As compared to conventional fuels, biodiesel has higher value of flash point and fire point which them better than conventional fuels.

Flash point of Pongamia biodiesel and mahua biodiesel is found to be 110°C and 204°C respectively. Fire point of Pongamia biodiesel and Mahua biodiesel are found to be 230°C and 185°C respectively.

Acid Value and Iodine Value

Acid value of Pongamia and Mahua biodiesel is found to be 0.46 mg KOH/gm and 0.5 mg KOH/gm respectively. Mahua biodiesel is found to have low acid value and iodine value which makes it beneficial for use in diesel engine because higher value of these both properties will create problem like knocking, corrosion in the nozzle of engine etc.

Iodine value is the measurement of unsaturations in fats or in oil. Higher the iodine value more will be unsaturation. Iodine value of pongamia and Mahua biodiesel is found to be 92.50 gm I_2/gm and 0.25 gm I_2/gm, respectively which indicate higher unsaturation in case of pongamia biodiesel.

Saponification Value and Free Fatty Acid

Higher saponification value cause soap formation. The saponification value and free fatty acid value of Mahua biodiesel is found to be low (130 mg KOH/gm, 0.08 mg KOH/gm,) to that of pongamia biodiesel (190 mg KOH/gm, 0.23 mg KOH/gm) which signifies the higher efficiency of Mahua biodiesel.

FTIR Analysis of Fatty Acid Methyl Esters (FAME)

The confirmation of biodiesel is done by analyzing the peaks which appeared in FTIR for pongamia and Mahua biodiesel with diesel fuel taken as reference.

The frequency of pongamia biodiesel (692.47) lies on the same peak to that of diesel frequency (671.25) having bond C≡C–H: C–H and alkynes as functional group. The vibration associated with this peak is bend. Others frequency for pongamia biodiesel is shown in Table 7.

Similarly, the frequency of Mahua biodiesel (723.33) was located on the same peak to that of diesel frequency (723.33) having bond C-H and alkanes as functional group. The vibration associated with this peak is rock. Others frequencies for Mahua biodiesel are shown in Table 8.

Table 3: Percentage yield of biodiesel from Pongamia and Mahua oils.

Oil Sample	Amount of oil taken (mL)	Amount of biodiesel produced (mL)	Yield of biodiesel (%)
Pongamia pinnata oil	200	146	75
Madhuca indica oil	200	165	84.5

Table 4: Kinematic viscosities of Pongamia pinnata and Mahua indica biodiesel at different set of temperature.

Kinematic Viscosity		
Temperature (°C)	Pongamia biodiesel (cSt)	Mahua biodiesel (cSt)
30	7.055	7.4139
35	6.396	7.6755
40	4.920	4.0
45	4.5398	5.4253
50	3.5988	5.1216

Table 5: Yield of Pongamia pinnata biodiesel and Madhuca indica biodiesel at different set of temperature.

S. No	Temperature	Maximum Yield (%)	
		Pongamia Biodiesel	Mahua Biodiesel
1.	40	51.20	55.80
2.	50	59.45	61.23
3.	60	75.00	84.50
4.	70	73.45	81.40
5.	80	72.30	77.65
6.	90	69.57	73.68

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Table 6: Physiochemical properties of Pongamia pinnata biodiesel and Madhuca indica biodiesel and their comparison with biodiesel standard (ASTM).

S. No.	Physicochemical Properties	Pongamia Biodiesel	Mahua Biodiesel	Biodiesel Standards (ASTM)
1	Density at 40°C (Kg/m^3)	860	872	870-920
2	Specific Gravity at 40°C	0.917	0.848	0.860 – 0.900
3	Saponification Value (mg KOH/gm)	190	130	191 - 202
4	Acid Value (mgKOH/gm)	0.46	0.05	0. 80 (max)
5	Free Fatty Acid (mg KOH/gm)	0.23	0.08	----
6	Iodine Value (gm I_2/gm)	92.50	85	82 - 98
7	Kinematic Viscosity at 40°C (cSt)	4.920	4.0	----
8	Cloud Point (°C)	7	6	-3 to 12
9	Pour Point (°C)	4	1	-15 to 10
10	Flash Point (°C)	110	204	----
11	Fire Point (°C)	230	185	130 (min)
12	pH	6.8	7.2	7
13	Ash Content	0.098	----	0.02 (max)

Table 7: FTIR analysis of Pongamia biodiesel with diesel fuel taken as a standard.

Pongamia Biodiesel Frequency	Diesel Frequency	Bonds	Functional Groups	Type of Vibration	Peak Intensity
692.47	671.25	C≡C–H: C–H	alkynes	Bend	Broad & Strong
723.33	723.33	C–H	alkanes	Rock	Medium
1363.72	1375.29	C–H	alkanes	Rock	Medium
651.12	1649.19	–C=C–	alkenes	Stretch	Medium
1741.78	1743.71	C=O	esters, saturated aliphatic	Stretch	Strong
2854.74	2856.67	C–H	alkanes	Stretch	Medium
2926.11	2924.18	C–H	alkanes	Stretch	Medium

Table 8: FTIR analysis of Madhuca indica biodiesel with diesel fuel taken as a standard.

Mahua Biodiesel Frequency	Diesel Frequency	Bonds	Functional Groups	Type of Vibration	Peak Intensity
723.33	723.33	C–H	alkanes	Rock	Medium
1396.5	1375.29	C–H	alkanes	Rock	Medium
1362.09	1460.16	N–O	alkenes	Stretch	Medium
1647.26	1649.19	N–H bend	1 amine	Stretch	Medium
1743.71	1743.71	C=O stretch	Esters, saturated aliphatic	Stretch	Strong
2926.11	2924.18	C–H	alkanes	Stretch	Medium

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a) Two layer formation b) Washing step c) Pongamia pinnata biodiesel

Figure 3: Biodiesel formation process from Pongamia pinnata oil.

a) Two layer formation b) Washing step c) Madhuca indica biodiesel

Figure 4: Biodiesel formation process from Madhuca indica oil.

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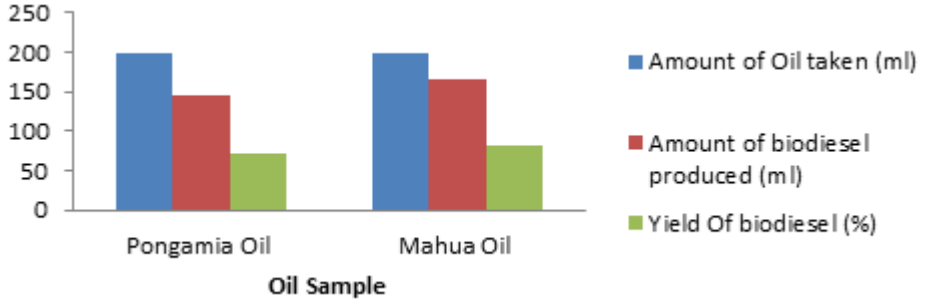

Figure 5: Qualitative Analysis of biodiesel yield obtained from Pongamia and Mahua oil.

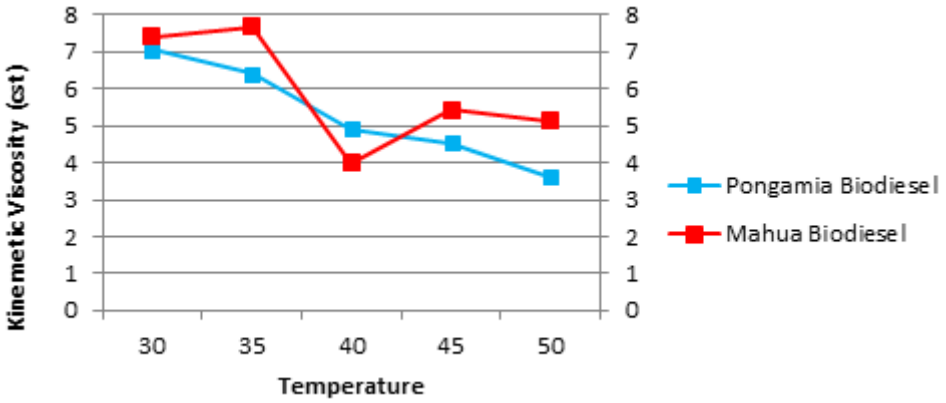

Figure 6: Kinemetic viscosity of pongamia and Mahua at different temperature.

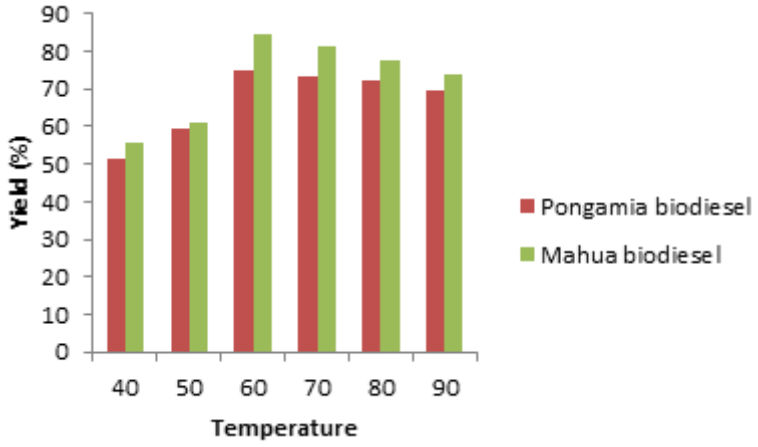

Figure 7: Yield of pongamia biodiesel and Mahua biodiesel at different temperatures.

CONCLUSIONS

The conversion into biodiesel was nearly 75% for Pongamia oil and 82.5% for Mahua oil by transesterification reaction. The effect of changing the reaction temperature on the yield of biodiesel was studied and maximum biodiesel yield is produced at 60ºC.

Their fuel property like specific gravity and cloud point were determined and compared with the ASTM standards. And it has been found that these values of Specific gravity, Flash point, Pour Point lies within the limits of ASTM standard. The flash point and fire points are high which is favorable for fuel transportation. The various factors which determine the quality of biodiesel such as flash point, pour point etc. have been determined and the quality of both the oils was good enough for them to be used as fuel in Biodiesel-based engines with a great performance and lower emission of greenhouse gases compared with fossil fuel. The

biodiesel is used mainly in the form of blends. Biodiesel so produced is environment friendly and can mimics as an alternative diesel engine fuel in future.

However, in future, the technology for biodiesel production needs further study in terms of purification process. Newly developed heterogeneous catalysts like (MgO and ZnO) should be used in place of homogenous catalyst (H_2SO_4 and KOH). Effective utilization of glycerol will contribute to the viability, commercialization and further focus on biodiesel production.

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