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Comparative Study on Properties of Methyl Ester of Cotton Seed Oil and Methyl Ester of Mango Seed Oil with Diesel

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Abstract- The use of fatty acid methyl esters (FAME), often referred to as biodiesel, instead of fossil diesel fuel is under consideration in order to increase the share of fuels from renewable sources and to reduce green house gas emissions. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and easily available. Fatty acid methyl esters have found to befit all these essential qualities. Fatty acid methyl esters derived from various vegetable oils / animal fats have gained importance as an alternative fuel for diesel engines and almost no modifications are required for using biodiesel. The research on alternative fuels for compression engine has become essential due to depletion of petroleum products and its major contribution for pollution, where vegetable oil promises best alternative fuel. Vegetable oils, due to their agricultural origin are able to reduce net CO2 emissions to the atmosphere. But the major disadvantage of vegetable oil is its viscosity which is higher than diesel. In this study, the Methyl Ester of Cotton Seed oil (MECSO) and Methyl Ester of Mango Seed oil (MEMSO) from non-edible oils of Cotton seed oil and Mango seed oil are prepared, their properties are compared in order to meet EN 14214/ASTM D6751 Standards for biodiesel and with the standards of diesel fuel.

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Strictly as per the compliance and regulations of :

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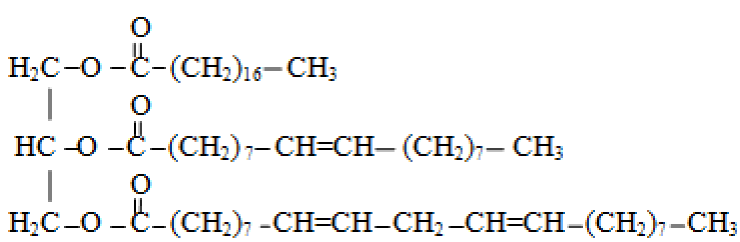
I. Introduction

Biodiesel is a domestically produced renewable fuel capable of strengthening India's energy security by reducing dependence on imported oil. The use of vegetable oil as a fuel for the compression engine is not a new idea. Rudolph Diesel used peanut oil to fuel the diesel engine during late 1800's.Petroleum based diesel fuel has been the fuel of choice for the diesel engine for many years due to abundant supply and low fuel prices. As long as the demand and cost of petroleum based fuel is growing rapidly and the present consumption pattern continues, these sources will be depleted in the near future. Time is needed to explore alternative sources of fuel energy. It has been found that the vegetable oils are promising fuels because their properties are similar to that of diesel and are produced easily and renewably from crops.

Conventional biodiesel mainly comes from edible and non-edible oils. Vegetable oil contains 98% triglycerides, having chemical structures as shown in below, small amounts of mono and diglyceride can also be present [1].



In most of the developed countries, biodiesel is produced from soya bean, rapeseed, sun flower, peanut, etc, which are essentially edible in Indian context. Among the various vegetable oil sources, non-edible oils are suitable for biodiesel production, because edible oils are already in demand and too expensive than diesel fuel. Many researchers are focused on non-edible oil which is not suitable for human consumption due to the presence of toxic components present in the oil. Further non-edible oil crops grow in the waste lands that are not suitable for cultivation. The cost of cultivation is much lower because these crops can still sustain reasonably oils that contain high free fatty acids. Among the non-edible oil sources, Jatropha, Karajan, Mahua, Neem, Cotton seed, Mango seed, Rice bran, etc., are identified as potential biodiesel source comparing with other sources, which has added advantages as rapid growth, higher seed productivity, suitable for tropical and subtropical region of the world [2].

Biodiesel is a chemically modified alternative fuel for use in diesel engines, derived from vegetable oils and animal fats. Biodiesel is produced commercially

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by the transesterification of vegetable oils with alcohol. Methanol or ethanol is the commonly used alcohols for this process. The direct use of alcohols as fuel causes corrosion of various parts in the engine, but the transesterification process solves this problem. In India, non-edible type oil yielding trees such as Linseed ,Castor, Karajan, Neem, Rubber, Jatropha, Kusum, Cotton, Mango and Cashew are available in large number. The production and utilization of these oils are low at present because of their limited end usage. Utilization of these oils / biodiesel as fuels in diesel engines are not only reduces the diesel usage, but also improves the rural economy.

Different biodiesels derived from different sources have been tested in diesel engines for several years. All these biodiesels perform differently in diesel engine in terms of performance, emissions and combustion. Because the physical and chemical properties of biodiesel derived from different sources are not the same, those properties have strong relation with the fatty acid composition of biodiesel. The structure of the fatty acid compounds can also affect other properties of biodiesel such as density, cetane number, heating value and low temperature properties. Several researchers have observed that the exhaust emissions are affected by the use of biodiesel. It is known that biodiesel fuel gives higher oxides of nitrogen (NO_x) or lower while HC, CO and PM emissions are essentially lower than that of diesel fuel [3].

II. Biodiesel Standards

Oil companies and vehicle manufacturers are actively working with biofuel extender producers to have agreed standards for transesterified vegetable oils suitable for blending with conventional diesel to ensure that the product meets the technical requirements of modern diesel engines. The minimum requirements for biodiesel blend extenders are specified in ASTM D6751 in USA and EN 14214 within Europe.

The regular mineral diesel is subject to the EN 590 standard and in 1997 the European Committee for standardization was given the task to develop a uniform standard for fatty acid methyl ester (FAME) and the result was the EN 14214 specification. The introduction of this standard in 2004 is valid for all member states of the European Union. EN 590 and ASTM D975 fuel specifications for petroleum based automotive diesel fuel currently a biofuel extender content up to 5% by volume (B5) or in US up to 20% by volume (B20), which if meets may not affect the vehicle manufacturer's warranty. The table given below lists the EN 14214 and ASTM D6751 standard particulars to biodiesel [4].

Table 1 : Properties of biodiesel as per EN 14214/ASTM D6751 standards

S.No	Property	Requirement by the Standard	
		EN14214	ASTM D6751
1.	Specific gravity	-	0.86 – 0.9
2.	Kinematic viscosity	3.5 – 5.0	1.9 – 6.0
3.	Flash point	> 101	> 130
4.	Fire point	-	-
5.	Cloud point	Report to customer	-3 to 12
6.	Pour point	-	-15 to 10
7.	Density	860 - 900	870 - 900
8.	Calorific value	-	35,000
9.	Cetane Number	51	48- 65

III. Preparation of Biodiesel

The non-edible oils selected for this study are cotton seed oil and mango seed oil. These two oils are converted into methyl esters by the transesterification process. Transesterification is otherwise known as "alcoholysis". It is the reaction between triglycerides of cotton seed oil / mango seed oil and methanol in the presence of potassium hydroxide (catalyst) leads to methyl ester of cotton seed oil / methyl ester of mango seed oil (Biodiesel) and a by product of glycerol.

The overall transesterification reaction is given by three consecutive and reversible equations as below:

$$\text{Triglyceride} + \text{ROH} \xrightleftharpoons{\text{Catalyst}} \text{Diglyceride} + R'COOR$$

$$\text{Diglyceride} + \text{ROH} \xrightleftharpoons{\text{Catalyst}} \text{Monoglyceride} + R''COOR$$

$$\text{Monoglyceride} + \text{ROH} \xrightleftharpoons{\text{Catalyst}} \text{Glycerol} + R'''COOR$$

The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides and of monoglycerides to glycerol. The overall chemical reaction of the transesterification process is,

$$\begin{array}{l} CH_2OOR_1 \\ | \\ CHOOR_2 \\ | \\ CH_2OOR_3 \end{array} + 3CH_3OH \xrightarrow{\text{(Catalyst)}} 3CH_3OOR_X + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Triglyceride Methanol Biodiesel Glycerin

As seen above, the transesterification is an equilibrium reaction in which excess alcohol is required to drive the reaction close to completion. The reaction takes place with maximum yield obtained at temperature ranging from 45 – 60ºC [5].

A laboratory-scale biodiesel production set-up was designed and fabricated in the laboratory as shown the figure 1. It consists of a motorized stirrer, straight coil electric heater and stainless steel containers. The system was designed to produce 5 litres of biodiesel. Temperature of the mixture of triglyceride, methanol and catalyst were maintained at about 55°C. Triglycerides is readily transesterified in the presence of alkaline catalyst at atmospheric pressure and at 55 to 60°C with an excess of methanol. The mixture at the end of reaction is allowed to settle. The lower Glycerol layer is drawn off, while the upper methyl ester layer is washed to remove entrained Glycerol and then processed further.

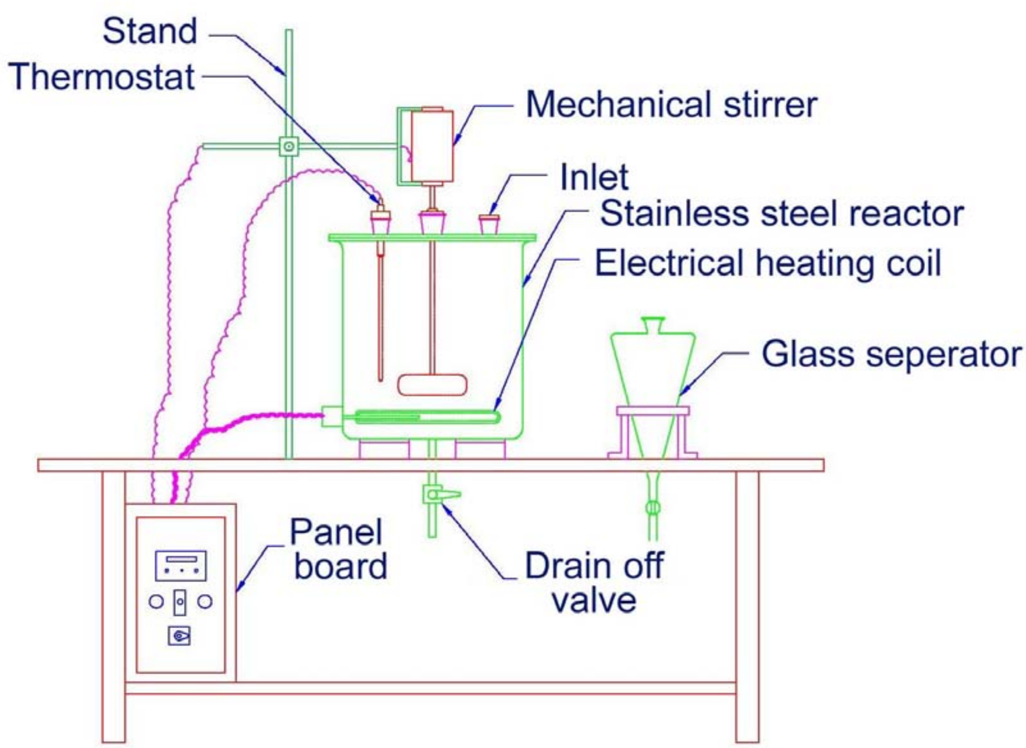

Figure 1 : Schematic of Biodiesel Plant

a) Transesterification of Cotton Seed oil

The transesterification process of cotton seed oil was performed using 13 gm of potassium hydroxide and 250 ml of methanol per litre of raw cotton seed oil. First, raw cotton seed oil was taken in a container and stirred with a mechanical stirrer and simultaneously heated with the help of a heating coil. The speed of the stirrer should be minimal till the temperature of the raw oil reaches 55ºC .Then the KOH was mixed with methanol separately in a beaker and stirred until they were properly dissolved. The solution was then added to the preheated cotton seed oil in the reactor and the reactor was closed with air tight lid. Now the solution was stirred at high speed of 650 rpm, care should be taken that the temperature does not exceed 60ºC as methanol evaporates at temperature of 65ºC. Also the KOH- alcohol solution was mixed with cotton seed oil only at 55ºC because heat generated when KOH - alcohol were mixed together and the temperature of the raw oil should be more than this when the mixing was done if the reactions have to take place properly. After the mixture was stirred for 30 minutes at a fixed temperature of 60ºC, the solution was transferred to a glass container where the separation of glycerin takes place and allowed to settle down for 15 hrs. Now the methyl ester of cotton seed oil (biodiesel) gets collected in the upper portion of the glass container whereas glycerin gets collected at the bottom portion and drain the bottom layer containing glycerin. Then the biodiesel was washed with water, again glycerin gets separated from biodiesel and was removed. The biodiesel was washed with water repeatedly for 4 to 5 times at a time interval of 1 hr until no glycerin was there in the biodiesel. Now the biodiesel was heated for 103 to 105ºC in order to remove water contained in it. Finally, the produced methyl ester of cotton seed oil (MECSO) was left to cool down and was ready for use. A maximum of 800 ml methyl ester of cotton seed oil (biodiesel) production was observed for 1 litre of raw cotton seed oil, 250 ml of methanol and 13 gm of potassium hydroxide at 60ºC.

b) Transesterification of Mango Seed oil

The transesterification process of mango seed oil was performed using 12 gm of potassium hydroxide and 200 ml of methanol per litre of raw mango seed oil. First, raw mango seed oil was taken in a container and stirred with a mechanical stirrer and simultaneously heated with the help of a heating coil. The speed of the stirrer should be minimal till the temperature of the raw oil reaches 55ºC. Then the KOH was mixed with methanol separately in a beaker and stirred until they were properly dissolved. The solution was then added to the preheated mango seed oil in the reactor and the reactor was closed with air tight lid. Now the solution was stirred at high speed of 600 rpm, care should be taken that the temperature does not exceed 60ºC as methanol evaporates at temperature of 65ºC. Also the

KOH- alcohol solution was mixed with cotton seed oil only at 55°C because heat generated when KOH - alcohol were mixed together and the temperature of the raw oil should be more than this when the mixing was done if the reactions have to take place properly. After the mixture was stirred for 30 minutes at a fixed temperature of 60°C, the solution was transferred to a glass container where the separation of glycerin takes place and allowed to settle down for 15 hrs. Now the methyl ester of mango seed oil (biodiesel) gets collected in the upper portion of the glass container whereas glycerin gets collected at the bottom portion and drain the bottom layer containing glycerin. Then the biodiesel was washed with water, again glycerin gets separated from biodiesel and was removed. The biodiesel was washed with water repeatedly for 4 to 5 times at a time interval of 1 hr until no glycerin was there in the biodiesel. Now the biodiesel was heated for 103 to 105°C in order to remove water contained in it. Finally, the produced methyl ester of mango seed oil (MEMSO) was left to cool down and was ready for use. A maximum of 850 ml methyl ester of mango seed oil (biodiesel) production was observed for 1 litre of raw mango seed oil, 250 ml of methanol and 12 gm of potassium hydroxide at 60°C.

IV. Analysis of Fuel Properties

The combustion, performance and emissions of CI engine mainly depend upon the properties of fuel used, among which specific gravity, viscosity, density, cetane number, flash point, fire point and calorific value are very important. The properties of MECSO and MEMSO are found and are quite close to that of diesel. So the MECSO and MEMSO can be used in existing diesel engines without any modifications.

a) *Specific Gravity*

Relative density is one of the most important properties of fuels, because injection systems, pumps and injectors must deliver the correct amount of fuel precisely adjusted to provide proper combustion [6]. Relative Density otherwise known as the specific gravity refers to the ratio of the density of a fuel to the density of water at the same temperature. The relative density of methyl ester of cotton seed oil, methyl ester of mango seed oil and biodiesel-diesel blends were measured by means of hydrometer. The specific gravity observed for MECSO and MEMSO were 0.8965 and 0.8952 respectively (Table 2).

b) *Kinematic Viscosity*

Viscosity is a key fuel property because it influences the atomization of a fuel upon injection into the combustion chamber and eventually the formation of soot and engine deposits. The viscosity of the methyl ester of cotton seed oil and methyl ester of mango seed oil are measured by redwood viscometer. The Kinematic viscosity of MECSO and MEMSO is nearer to that of diesel.

c) *Density and Heating value*

The density of methyl ester of cotton seed oil and methyl ester of mango seed oil at 15°C is 895.7 kg/m^3 and 894.3 kg/m^3 respectively. Higher heating value is a measure of the energy produced when the fuel is burnt completely, which also determines the suitability of biodiesel as an alternative to diesel fuel. Table 2 shows the gross calorific value of MECSO and MEMSO which is closer to diesel.

d) *Cetane Number (CN)*

The CN is one of the common indicators of diesel fuel quality. It measures readiness of the fuel to auto ignite when injected into the engine. ASTM standard test method D 613 states that, for fuels with cetane numbers in the range of 44 to 56, the repeatability should be within 0.7 to 0.9 cetane number units [7]. The cetane number of MECSO and MEMSO was determined as 52.

Table 2 : Properties of Diesel, MECSO and MEMSO

S.NO	PROPERTY	DIESEL	BIODIESEL	
			MECSO	MEMSO
1	Specific gravity @ 15°C	0.8290	0.8965	0.8952
2	Kinematic Viscosity @ 40°C in cSt	2.57	5.8	5.6
3	Flash point °C	53	162	168
4	Fire point °C	59	173	174
5	Cloud Point °C	bel -8	-2	0
6	Pour point °C	bel-14	-5	-7
7	Density @ 15°C (kg/m^3)	828.1	895.7	894.3
8	Gross Calorific Value (kJ/kg)	44,680	40,610	40,874
9	Cetane Number	51	52	52

e) *Important Temperatures*

Pour Point and Cloud Point are important for cold weather operations of the IC engine. For satisfactory working, the values of both should be well below the freezing point of the oil used. The cloud point and pour point observed for MECSO and MEMSO were

-2°C,-5°C and 0°C,-7°C respectively (Table 2). Flash point is an important temperature from a safety point of view. The flash point of the biodiesel was set to 98°C so as to meet the minimum requirement of non-hazardous fuel certification according to ASTM D6751 standard test method. The flash point and fire point observed for MECSO and MEMSO were 162°C, 173°C and 168°C, 174°C respectively (Table 2).

V. Fatty Acid Composition

The fatty acid composition of the oils seems to have an important role in the performance of the biodiesel in diesel engines [8]. Based on the fatty acid composition and many other parameters, the EU biodiesel specifications will be mandatory to limit the oxidative stability, as it may be a crucial parameter for injection pump performance [9]. Moreover, the stability of the fuel is a quality parameter established by the ANP- National Petroleum Agency in Brazil, being its evaluation and control necessary [10].

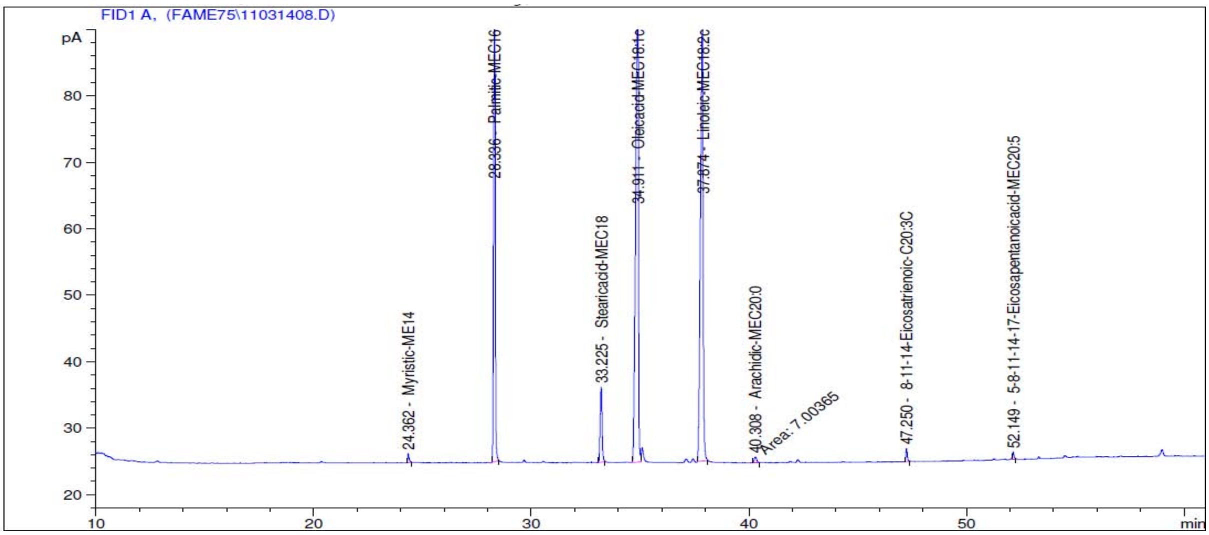

Figure 2 : GC-FID Analysis for Methyl Ester of Cotton Seed Oil

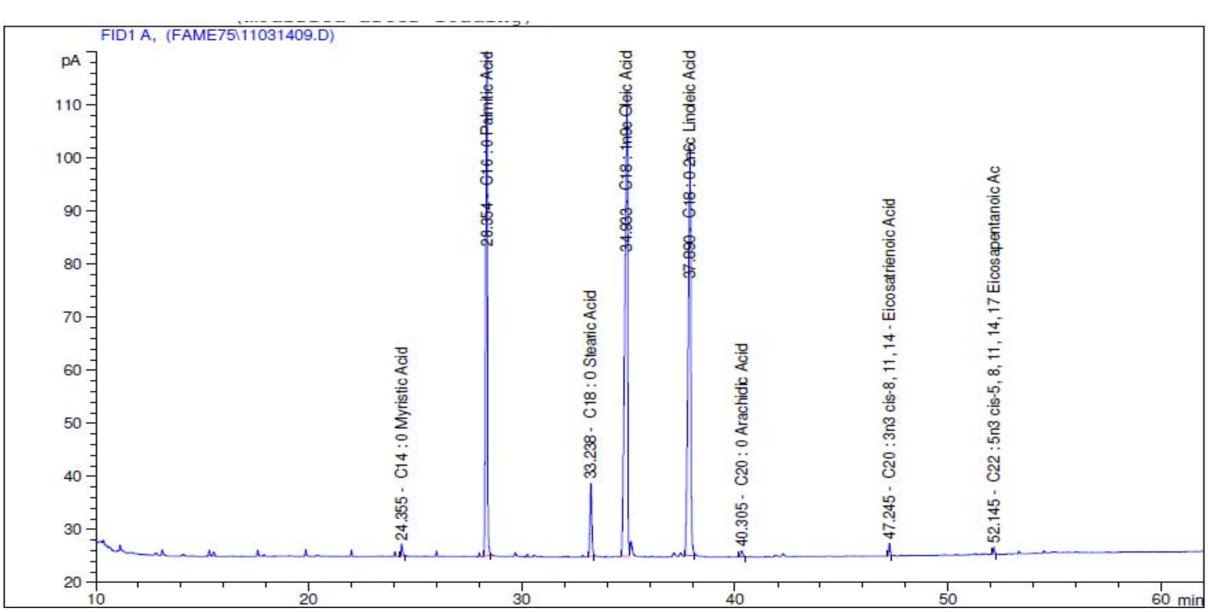

Figure 3 : GC-FID Analysis for Methyl Ester of Mango Seed Oil

Vegetable oils are natural products consisting of ester mixtures derived from glycerol (triglyceride), whose chains of fatty acid contain about 14 to 20 carbon atoms with different degrees of unsaturation. The transesterification reaction consists in the conversion of the triglyceride molecules, by means of the action of short chain alcohol, i.e., methanol, ethanol into the corresponding fatty acid esters. According to the source of oilseed, variations in the chemical composition of the vegetable oil are expressed by variations in the molar ratio among different fatty acids in the structure [11].

The prepared biodiesel i.e., methyl ester of cotton seed oil and methyl ester of mango seed oil were analyzed by GC-FID to determine the composition of fatty acids (Figure 2 & 3). The biodiesel is mainly formed by transesterification of saturated and monounsaturated fatty acids while the remaining polyunsaturated and some bulk saturated fatty acid are responsible for high viscosity of the biodiesel. The higher level of unsaturated fatty acid reduces fuel quality, because of its easy oxidation [12]. As a rule saturated fatty acid such as16:0 or 18:0 are stable than unsaturated ones like 18:1, 18:2 and 18:3 which decreases the fuel quality [13]. The result also shows that methyl esters of biodiesel obtained from transesterification has more percentage of saturated fatty acids with less percentage of unsaturated fatty acids. The presence of saturated fatty acid in the obtained biodiesel leads to high viscosity, high cetane number and better biodiesel stability. The measured values of fatty acids present in the methyl ester of biodiesel are given in Table 3.

Table 3 : Measured values of Fatty acids in the methyl esters of biodiesel

Type	Fatty Acids			Methyl ester of Cotton Seed oil	Methyl ester of Mango Seed oil
UNSATURATED	1.	Oleic	18:1	38.34	37.29
	2.	Linoleic	18:2	33.87	32.15
	3.	Palmitoleic	16:1	<0.01	<0.01
SATURATED	4.	Lauric	12:0	<0.01	<0.01
	5.	Palmitic	16:0	21.87	24.73
	6.	Stearic	18:0	4.12	4.07
	7.	Arachidic	20:0	0.46	0.42
	8.	Myristic	14:0	0.40	0.49
	9.	Margaric	17:0	<0.01	<0.01

VI. Conclusions

Cotton seed oil and Mango seed oil are chosen as potential non-edible vegetable oil for the production of biodiesel. Here the biodiesel were prepared from cotton seed oil and mango seed oil by transesterification process. Biodiesel specific gravity, viscosity, density, cetane number, flash point, fire point and calorific value were according to the EN 14214/ASTM D6751 Standards for biodiesel. The calorific values of biodiesel are found to be slightly lower than that of diesel and their properties are quite close to diesel. The fatty acid compositions obtained from GC-FID data were according with the literature. So the methyl ester of cotton seed oil and methyl ester of mango seed oil can be used in the existing diesel engines without any modifications.

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