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Comparative Studies of Properties of Diesel and Bio-Diesel Produced from Non-Edible Oils

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Abstract

Bio-diesel is the mixture of alkyl esters of long chain fatty acid. These esters can be obtained from edible or non-edible organic oils by trans-esterification with methanol/ethanol. The trans-esterification can be carried out chemically or enzymatically. In this article, five comparative studies of different non-edible organic oils (karanj, jatropha, linseed kalatil and castor) have been carried out for a trans-esterification reaction in presence of KOH and NaOH catalysts to produce bio-diesel. The use of methanol and ethanol as solvents for five oils is mentioned to evaluate the better ester production. Ethyl ester and methyl ester are found to give appreciably more yield with KOH catalyst and NaOH, respectively. Comparative study with diesel was carried out by producing the bio-diesel from jatropha, karanj, castor, linseed and kalatil oils. The bio-diesel ester characteristics for their physical and fuel properties are obtained by studying the parameters viz. calorific value, viscosity, acid value, peroxide value, saponification value, ash content and water content and density. The comparative values of these parameters are found to be nearly same with the petroleum diesel except the little lower calorific value and higher values of viscosity. The viscosity values varied nearly four times higher in kalatil methyl ester and 10 times higher in castor methyl ester. The other ester values were found between these values. From a study carried out for 20 days and six months old samples kept open to environment, it is found that the bio-diesel degradation effects are different in all different methyl and ethyl esters. Due to the higher oxidative properties of different esters compared to diesel, is not good as shown by acid value, peroxide value and saponification value. The acid values are high nearly 34 to 820% in six month stored samples than 20 days stored samples. On the other hand, the peroxide values vary from 30 to 111% more in six months old samples than 20 days old samples. The saponification values are also found higher of range 60 to 247% in six months old samples in comparison to 20 days old samples.
Key words : Bio-diesel, Trans-esterification, Methyl ester, Ethyl ester.

The rising cost of petroleum products burden the economies of developing countries. Therefore, there is a need to search for the required petroleum product. Bio-diesel is one of the important fuels of the future and continued and increasing use of petroleum will also intensify local air pollution and magnify the global warming caused by CO_2 (1). Therefore, to overcome this problem, vegetative oils are used as diesel fuels from time to time. At the very beginning, Rudolf Diesel tested vegetative oil as a fuel for his engine. But the use of vegetable oil as petroleum diesel creates some problem of cold weather operating and unsaturated compounds present in the vegetative oil result into polymer formation (like gum) in the combustion chamber which is carried into the lubricating system, clogging the oil filter with the resultant reduced flow (2). With the advent of cheap petroleum, appropriate crude oil fractions are refined to serve as fuel as diesel. Crude oils are primarily water insoluble, hydrophobic substances and are made up of one mole of glycerol and three moles of fatty acids (3). By the method of trans-esterification, the methyl or ethyl ester are obtained from the crude oils as a bio-diesel, the reaction catalyzed with an alkali like

Table 1. The amount of bio-diesel and glycerol extracted from different non-edible oils.

Non-edible oils 1 liter each	Alcohol 200 ml	Catalyst	Bio-diesel	Glycerol
Karanj oil	Ethanol	KOH	900 ml	200 ml
Jatropha oil	Ethanol	KOH	900 ml	200 ml
Linseed oil	Methanol	NAOH	900 ml	200 ml
Kalatil oil	Methanol	NAOH	1000 ml	100 ml
Castor oil	Methanol	NAOH	700 ml	400 ml

KOH or NaOH and the glycerol obtained as by- product (4). This bio-diesel is bio-degradable and non-toxic, with low emission profiles and environmentally beneficial (1). Bio-diesel fuel also reduces the level of pollutants such as CO, aromatics, polycyclic aromatic hydrocarbons and partially burned or unburned hydrocarbon ermission as compared to diesel. But the use of essential edible oil for the isolation of bio-diesel as a substitute for diesel may lead to a concept of self-sufficiency in plant edible oil production, which India has not yet attained. There is an abundance of forest and tree borne and wild plant produced non-edible oil available in India like karanj, castor, linseed, jatropha, kalatil, but attempt has not been made extensively to use these non-edible oils as a substitute to diesel. In this present article, above mentioned non-edible oils can be used to obtain ethyl and methyl ester as bio-diesel. A comparable study of parameters viz., calorific value, viscosity, ash content, water content, acid value, saponification value, peroxide value, and density of fuel properties has been mentioned between isolated bio-diesel and the petroleum diesel to understand the better combustion efficiency of bio-diesel.

Methods

Process of Bio-Diesel Production

Bio-diesel is isolated from the different oils of karanj, linseed, kalatil, castor and jatropha. Bio-diesel is extracted by the same process of trans-esterification of oil. Trans-esterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis. This process has been widely used to reduce the viscosity of triglycerides. The trans-esterification reaction is represented by the general equation

Triglycerides+ROH catalyst → Diglycerides + R^*COOR
Diglycerides+ROH catalyst → Monoglycerides + R^*COOR
Monoglyceride + ROH catalyst → Glycerol + R* COOR

It is the reaction of oil with an alcohol to form esters and glycerol and the reaction rate and yield is catalyzed by KOH or NaOH. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side.

Process Variable in Trans-Esterification

Bio-diesel is manufactured by the trans-esterification of fats and oils. Triglycerides are readily trans-esterified batch-wise in the presence of alkaline catalyst at atmospheric pressure and temperature of approximately 60—70 C with an excess of methanol. Alkali catalysts are the most effective catalysts compared to acidic catalyst. Another important variable affecting the yield of ester is the molar ratio to vegetable oil. A molar ratio of 5 : 1 is normally used in industrial processes to obtain methyl ester yield higher than 98% by weight. Peterson et al., stated that the practical range of molar ratio is from 3.3 to 5.25 : 1 methanol to oil. The mixing effect is most significant during the slow rate region of the trans-esterification reaction. It is observed that after adding methanol and catalyst to the oil, 45—60 min stirring helps in higher rate of conversion and recovery. It has been reported in a commonly used single stage process, a

Table 2. Calorific value, ash content and water content.

Fuel properties	Linseed methyl ester	Kalatil methyl ester	Castor methyl ester	Karanj ethyl ester	Jatropha ethyl ester	Diesel
Calorific value (kcal/kg)	8,438.4	7,922.3	9,808.5	9,997.2	10,689	10,770
Ash content	0.03	0.019	0.08	0.03	0.04	0
Water content	0.47	0.34	0.9	0.84	0.6	0

Table 3. Density of ester at different temperature (C).

Esters	40	50	60	70	80	90	100	Diesel
Karanj ethyl ester	0.90	0.89	0.89	0.88	0.88	0.88	0.87	0.84
Linseed methyl ester	0.97	0.77	0.77	0.76	0.75	0.75	0.74	
Kalatil methyl ester	0.89	0.87	0.87	0.86	0.85	0.85	0.84	
Castor methyl ester	0.77	0.77	0.77	0.76	0.75	0.74	0.74	
Jatropha ethyl ester	0.90	0.89	0.87	0.87	0.86	0.85	0.84	

Table 4. Viscosity of ester at different temperature (C).

Esters	40	50	60	70	80	90	100	Diesel
Karanj ethyl ester	54.9	33.8	25.8	19.2	13.5	11.1	10.2	2.8
Linseed methyl ester	47.1	31.3	22.6	17.2	11.2	10.1	9.5	
Kalatil methyl ester	21.4	19.1	17.2	15.9	11.7	9.5	8.1	
Castor methyl ester	62.0	54.7	49.5	35.4	23.1	19.3	15.6	
Jatropha ethyl ester	24.2	20.6	18.6	17.1	16.2	15.3	12.62	

period of one hour is required to achieve 98% conversion of rapeseed oil to methyl esters (3).

Impurities in the oil affect the conversion level considerably. It is reported that about 65—84% conversion into ester using crude vegetable oil has been obtained as compared to 94—97% yield refined oil under the same conditions.

Characteristics of Bio-Diesel

The acid values and peroxide values are determined for understanding the storage ability of bio-diesel. Acid values of bio-diesel are determined as the percentage of free fatty acid present in oil. Free fatty acid in oil is estimated by titrating it against KOH in presence of phenolphthalein indicator. Peroxide value is the peroxide present in oil that is determined by titrating against sodium thiosulfate in presence of KI and starch is used as an indicator. The gross heating values of bio-diesel are determined by bomb calorimeter. A weight sample contained in capsule is burnt in oxygen in the bomb calorimeter and the heat value of sample is calculated. Gross heating value of bio-diesel is expressed in kcal/kg. Density of bio-diesel is determined by means of capillary stopper relative density bottle of 25 ml capacity at different temperature. Density is expressed in g/ml. Viscosity of bio-diesel is determined by Redwood viscometer No. 1. This apparatus is based on the principle of measuring the time of gravity flow (in seconds) of a fixed volume (25 ml) of fluid through the specified hole made in an agate piece. Bio-diesel is heated to different temperatures up to a maximum of 110 C. Kinematics viscosity in centistokes (cSt) is calculated from the time unit. Saponification value is the amount (mg) of alkali required to saponify a definite quantity (1 g) of bio-diesel. This value is useful for a comparative study of the free fatty acid chain length in bio-diesel.

Results and Discussion

The five different non-edible oils are screened for trans-esterification by using KOH and NaOH solvents. The fuel properties of bio-diesel from selected oils are compared with diesel. The esters are not found good enough with methanol in karanj and jatropha oils in comparison to ethanol. Therefore, the good solvents are identified and used for selected oils to get enhanced production of esters. The quantitative study of ester and glycerol production is summarized in Table 1. It shows that nearly 100% production of ester of crude oil is transformed from the oil of kalatil. The glycerol obtained from this oil is negligible (about 100 ml/liter). Esters from karanj, jatropha and linseed oils are obtained in same proportion as 90% of crude oil quantity. Ester obtained as methyl ester from castor oil is 70%. The glycerol quantities and losses are found same after the esterification of karanj, jatropha and linseed oils. But, the glycerol quantities are obtained high with castor oil. The glycerol is supposed to be contaminated in the bio-diesel and presence of lesser amount of glycerol in the oil reflects the efficiency of this oil to produce better bio-diesel.

During extraction of bio-diesel in the form of ethyl ester from the oils of karanj and jatropha, the catalyst KOH has been given better results with ethyl alcohol during trans-esterification reaction. It is because of KOH is weaker alkaline than NaOH, while methyl alcohol is slightly acidic than ethyl alcohol. Therefore,

Table 5. Acid value, peroxide value and saponification value of esters.

Fuel properties	Linseed methyl ester	Kalatil methyl ester	Castor methyl ester	Karanj ethyl ester	Jatropha ethyl ester
Acid value (mg KOH/g)	4.4	0.5	1.2	5.4	6.1
After six months	5.9	4.6	4.6	8.4	9.7
Increase (%)	34.0	820.0	283.0	55.55	59.01
Peroxide value (milli equivalent peroxide/kg sample)	90	100	50	30	150
After six months	190	130	70	40	220
Increase (%)	111.11	30	40	33	46.66
Saponification value	213.1	129.0	147	134	123.4
After six months	342.2	426.3	398.3	339.4	429.1
Increase (%)	60.58	230.46	170.95	153.28	247.73

NaOH as being stronger alkali, the reaction is faster and more compatible with methyl alcohol. Methyl ester production from the oils of linseed, kalatil, and castor catalyzed by NaOH give better results. It may be said that the trans-esterification in the oils of linseeds, kalatil and castor require some acidic media, which is provided by methyl alcohol. Earlier it is reported that ethanol and other primary alcohols are somewhat weaker acidic compared to water while methanol is a slightly stronger acid. A KOH is used to find the methyl ester which again dries by anhydrous sodium sulfate. When sodium hydroxide and methanol solution are added to the melted beef tallow in the reactor and stirred, the stirring time is insignificant.

Esters are characterized for their fuel properties including density, viscosity, peroxide value, saponification value, acid value, ash content, water content, and gross heat of combustion similar to those of diesel. However, bio-diesels are considerably less volatile than the conventional diesel fuels (2).

Bio-diesels have lower calorific value than the diesel ranging from 7,922.32 kcal/kg to 10,770 kcal/kg of esters obtained from the oils of kalatil, linseed, castor, karanj, jatropha, (Table 2). It has been reported that bio-diesel having lower calorific value than diesel may be better owing to higher density of bio-diesel and higher combustion efficiency. The lowest ash content is estimated in kalatil (0.019%) which is followed by linseed (0.03%), karanj (0.03%), jatropha (0.04%) and castor (0.08%) esters. Ash is controlled to ensure that all the catalyst used in the trans-esterification process is removed. Lowest amount of the ash indicates the better performance of bio-diesel. The presence of water content in the bio-diesel makes it susceptible to growing microbes which can clog fuel filter. The lowest water content is found in kalatil (0.34%) which is followed by linseed (0.47%), jatropha (0.6%), karanj (0.84%) and castor (0.9%) (Table 2).

The density of different esters decreases with increase in temperature as shown in Table 3. Linseed and castor methyl ester have lower density (0.79 and 0.77 g/ml, respectively) as compared to other esters and petroleum diesel and remain lowest up to 100°C temperature. While the density of other esters such as kalatil, and jatropha have density (0.84 g/ml at 100 C) that is near about the density of petroleum diesel at room temperature. The density is found ranging from 0.74 to 0.87 g/liter of the esters obtained from castor, linseed, petroleum diesel, kalatil, jatropha and karanj, respectively. The density of bio-diesel as compared to the petro-diesel is lower which indicate combustion efficiency of bio-diesel. Increased combustion efficiency results in lower emission of unburnt hydrocarbons (1).

The fuel viscosity controls the characteristics (droplet size, spray) of injection from the injector. Viscosities of all the ethyl and methyl esters are found highest at 40° C which decrease with increase in temperature. At 40 C temperature viscosities are 21.42 of kalatil methyl ester which is followed by 24.21 jatropha ethyl ester, 47.4 of linseed methyl ester, 54.9 of karanj ethyl ester and 62.0 of castor methyl ester. With increase in temperature, the viscosities of all esters decrease and lowest viscosities are determined at 100 C. At 100 C the lowest viscosity is found in kalatil methyl ester (8.4) which is followed by linseed methyl ester (9.6), karanj ethyl ester (10.1), jatropha ethyl ester (12.6) and castor methyl ester (15.7) (Table 4). The viscosity of esters goes to high level, and hence, it is important to control it within an acceptable level to avoid negative impact on fuel injection system performance.

The degree of peroxide formation and the time taken for the development of rancidity differ among the oils. Peroxide value measured for the different fatty acid esters range from 3—150 milli equivalent peroxide/kg in karanj, castor, linseed, kalatil and jatropha, respectively. Karanj has the lowest value (30 milli equivalent, peroxide/kg) followed by castor (50 milli equivalent peroxide/kg), linseed (90 milli equivalent peroxide/kg), kalatil (100 milli equivalent peroxide/kg) and jatropha (150 milli equivalent peroxide/kg). But after six months of storage, peroxide formation increases to 33,40,30,111 and 46%, respectively. The peroxide formation in linseed ester is too much which directly influences the storage capacity of bio-diesel isolated from linseed oil while the peroxide degradation of kalatil bio-diesel is low and can be stored for a long time without changing its properties (Table 5).

Free fatty acid content in oil along with the triglyceride ranges from 0.5 to 6.1 (mg KOH/gm) (Table 5). The lowest amount of free acid content is found in kalatil methyl ester (0.5 mg KOH/g) which is followed by castor methyl ester (1.2 mg KOH/g), linseed methyl ester (4.4 mg KOH/g), karanj ethyl ester (5.4 mg KOH/g) and jatropha ethyl ester (6.1 mg KOH/g). But on storing these fatty esters up to six months, the change in acid value are determined and found manifold increase in acid value content. In kalatil oil ester, the acid value increases about 820% which is followed by castor oil methyl ester (283%), linseed (34%), karanj (55.55%) and jatropha (59.01%). The free fatty acid content reflects the presence of fatty acid in biodiesel which increases during storage. The high acid number can cause damage to injector and also results in deposits in fuel systems and can affect the life of fuel pump and filter.

Saponification is the amount (mg) of alkali required to saponify a definite quantity (1 g) of an oil to compare the fatty acid chain length. The saponification value of jatropha ethyl ester is lowest i.e. 123.4 mg KOH/g followed by kalatil methyl ester (129.0 mg KOH/g), karanj ethyl ester (134.0 mg KOH/g), castor methyl ester (147.0 mg KOH/g) and linseed methyl ester (213.1 mg KOH/g), respectively. But after six month of storage, the saponification value increases about 247% in jatropha which is followed by 230% increase in kalatil, 155% in karanj, 170% in castor and 160% in linseed ester (Table 5). This indicates that the requirement of alkali in bio-diesel extraction from caring is lowest which may reduce the alkality of the diesel and may influence the cost of bio-diesel.

Conclusion

The following conclusions are made : Kalatil shows better ester separation (in 1 liter oil) and lower viscosity comparison to other oils; KOH shows better performance in ethyl ester formation while NaOH is better in methyl ester formation; linseed methyl ester and karanj ethyl ester show better performance due to lowest acid value, saponification value, density and free acid content than the others; and jatropha and karanj show better calorific value and linseed shows lowest density in comparison to other oils.

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