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NOTE

Evaluation of Properties and Storage Stability of *Madhuca indica* Biodiesel

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Abstract: Mahua Oil (MO) is an underutilized non-edible vegetable oil, which is available in large quantities in India. In the present work, biodiesel was derived from the MO by the transesterification process. The fuel properties of the MO biodiesel were found to be within the limits of biodiesel specifications of many countries. The chemical nature of biodiesel makes it more susceptible to oxidation during long-term storage which leads to degradation of fuel properties that can compromise fuel quality. The effect of long storage condition on the stability of the MO biodiesel was studied in the present work. The biodiesel samples were stored in plastic containers at room temperature. The study was conducted for a period of 12 months and the test sample was kept in the darkness. From the experimental results, it was observed that the acid value and viscosity increases with the storage time, but the iodine value decreased with increasing storage time. This is due to the presence of the double bond in the molecule of the biodiesel which produce a high level of reactivity. This high level reactivity produces formation of hydroperoxides, soluble polymers and other secondary products. From the experimental results, a slight difference in the acid value, iodine value and viscosity of the MO biodiesel stored for a period of 30 days was observed. But after this period, the differences were significant.

Key words: alternative fuel, mahua oil, transesterification, properties, storage

1 INTRODUCTION

During recent years high activities can be observed in the field of alternative fuels, due to supply of petroleum fuels strongly depends on a small number of oil exporting countries. In the year 2004-2005, India imported 75% of crude oil from other countries, to meet the energy requirements. The demand for diesel and gasoline increased drastically in the year 2008-2009. It has been estimated that the demand for diesel will be 66.90 million metric ton for the year 2011-2012. Biodiesel and alcohol are being considered to be supplementary fuels to the petroleum fuels in India. These biofuels are being looked to provide employment generation to rural people through plantation of vegetable oils and can be beneficial to sugarcane farmers through the ethanol program[1]. Few researchers examined the fatty acid profiles of seed oils of 75 plant species having 30% or more fixed oil in their seed. They reported that the fatty acid methyl esters of oils of 26 species were found most suitable for use as biodiesel and they meet the major specification of biodiesel standards of USA, Germany and Europe[2].

Mahua name for a medium to larger tree, madhuca longifolia of family sapotaceae with wider and round canopy. It is a slow growing species, attains a mean height of 0.9 to 1.2 m at the end of the fourth year. It may attain a height up to 20 m. The variety latifolia is common throughout the Indian sub-continent. As a plantation tree, mahua is an important plant having vital socio-economic value. This species can be planted on roadside, canal banks etc on commercial scale and in social forestry programmes, particularly in tribal areas. The drying and decortification yield 70% kernel on the weight of seed. The kernel of seed contains about 50% oil. The oil yield in an expeller is nearly 34-37% and the fresh oil from properly stored seed is yellow in color[3]. Figure 1 shows the mahua tree, seeds and oil expeller used for oil extraction. The seed and oil potential

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of this tree in India are 500 and 180 million ton respectively[4].

Shashikant *et al.*[5] produced biodiesel from the MO using response surface methodology and optimized the process variables. Purnanand *et al.*[6] investigated the cold flow properties of biodiesel fuel obtained from MO with and without pour point depressants towards the objectives of identifying the pumping and injecting of the MO biodiesel in compression ignition engines under cold climates. From the experimental results, they concluded that the ethanol blended biodiesel is totally a renewable, viable alternative fuel for improved cold flow behavior and better emission characteristics without affecting the engine performance. Raheman *et al.*[7] used the blends of MO biodiesel and diesel as fuel in a Ricardo E6 diesel engine. From the experimental results, they reported that the B20 blend results in reductions in exhaust emissions and brake specific fuel consumption together with increase in brake power and brake thermal efficiency. Sukumar *et al.*[8,9] work also gave the same results.

Generally, vegetable oil contains fatty acids (palmitic, stearic, oleic, linoleic, lignoceric, eicosenoic, arachidic and behenic). Of these, mahua oil contains the saturated fatty acids palmitic (hexadecanoic acid) and stearic (octadecanoic acid) and the unsaturated acids oleic (octadec-9-enoic acid) and linoleic (9,12-octadecadienoic acid). The fatty acid composition of the MO is given in Table 1. Linoleic and olenic acids, with two and one double bonds, respectively, oxidize readily. Both are found at relatively high levels in the MO. The methylene groups adjacent to the double bonds are particularly susceptible to free radical attack. Multiple double bonds on the same fatty acid chain are more susceptible to oxidation than would be indicated by the number of double bonds alone. Hence the MO biodiesel is highly unsaturated and this makes it very prone to oxidation.

Fig. 1 a) Mahua Tree b) Mahua Seeds c) Oil Expeller.

Table 1 Fatty Acid Composition of MO.

Fatty Acid	Formula	Structure	Weight %
Arachidic	$C_{20}H_{40}O_2$	20:00	0.00 − 3.3
Linoleic	$C_{18}H_{32}O_2$	18:02	8.9 − 13.7
Oleic	$C_{18}H_{34}O_2$	18:01	41.0 − 51.0
Stearic	$C_{18}H_{36}O_2$	18:00	20.0 − 25.1
Palmitic	$C_{16}H_{32}O_2$	16:00	16.0 − 28.2

Abdul *et al.*[10] studied the impact of oxidized biodiesel on engine performance. They compared the effect of oxidized biodiesel with the unoxidized biodiesel and diesel. They reported that the oxidation of the biodiesel can cause the fuel to become acidic and to form insoluble gums and sediments that can plug fuel filters. Also they reported that the oxidized biodiesel significantly affects the performance of the engine. Gerhard reviewed the factors that influence the biodiesel oxidative stability and their interaction. They reported that the oxidation of fatty acid chains is a complex process that proceeds by a variety of mechanisms[11]. McCormick examined the factors impacting the stability of biodiesel samples collected as part of a 2004 nationwide fuel quality survey in the United States of America. He reported that the polyunsaturated content (or oxidizability) has the largest impact on both increasing insoluble formation and reducing induction time[12]. Gerhard analyzed the biodiesel oxidization using Nuclear Magnetic Resonance. They reported that the acid values and kinematic viscosity of the biodiesel increased with time and surface area[13]. The biodiesel oxidation affects its quality and contributes to the malfunctions of fuel system and engine components. Hence there is a need to evaluate the biodiesel stability.

The purpose of the present work is to determine the fuel properties of MO biodiesel and to study its storage stability. The fuel properties of MO biodiesel were determined as per ASTM procedures and the storage stability was studied over a storage time of 12 month.

2 EXPERIMENTAL

2.1 Materials

The MO is underutilized and non-edible oil and hence selected for biodiesel production. The double filtered and refined MO was used for the present study. Table 2 shows the characteristics of the MO. Methanol was chosen as the alcohol used for the transesterification of the MO, because of its low cost. Sodium hydroxide is very well accepted and widely used catalyst because of its low cost and high product yield, hence it was used as catalyst for the present work. The methanol and sodium hydroxide were analytical reagent grade and purchased from Merck Chemical Company, India.

The biodiesel sample (3000 mL) was stored in plastic containers, at room temperature. The study was conducted for a period of 12 month. At regular intervals, samples

Table 2 Characteristic of MO.

Property	Value
Acid Value (mg KOH / g of oil)	16
Refractive Index	1.456
Saponification Value	190
Iodine Value	59
Colour	Dark yellow

were taken out periodically (30 day), to measure the acid value, viscosity, density and iodine value.

2.2 Apparatus

The transesterification reaction was carried out in a round bottom flask of 500 mL capacity equipped with a reflux condenser. A hot plate with magnetic stirrer arrangement was used for heating and stirring the mixture. The mixture was stirred at the same speed for all test conditions. For the uniform heating of the mixture, a water bath arrangement was made to heat the flask. The transesterification setup is shown in Fig. 2. During the experiment, 200 mL of MO was poured into the flask and heated to 60℃. The homogenous mixture of 60 mL of methanol and 1% (wt of the oil) of sodium hydroxide were added to the preheated MO. This mixture was stirred for 120 min. After the reaction, the products were poured into a 500 mL separating funnel and after separation, two layers were observed. The top layer containing esters were removed and washed with warm water, to wash out impurities like soap and other residues. Finally the methyl esters were heated above 100℃, to remove the moisture.

2.3 Measurements

The fuel properties of the MO biodiesel were determined as per ASTM procedures.

Fig. 2 Transesterification Setup.

3 RESULTS AND DISCUSSION

3.1 Properties of fuel

The important properties of the MO and MO Biodiesel (MOB) were determined and shown in Table 3. All the properties of the MOB were found to be within the limits of biodiesel specifications of many countries. If MO is used as sole fuel in diesel engine, the high viscosity of MO may results in increased droplet size, poor atomization and poor combustion. Therefore, viscosity was considered as one of the indices for fuel quality. The viscosity of MO is reduced from 27.63 to 4.85 cSt, due to transesterification. The low viscosity indicates the MO's ability to flow, which is increased to a significant extent by transesterification. Density of the biodiesel was included as it will affect the biodiesel mass flow per stroke of the injection pump plunger and, hence, will affect the power output of the engine. The cetane number of the MOB also satisfies the fuel standard. The higher flash point of the MO biodiesel indicates that the overall flammability hazard of MO biodiesel is much less than that of conventional diesel.

Table 3 Properties of MO, MO Biodiesel and Diesel.

Property	MO	MOB	Diesel	USA ASTM	Europe EN	German DIN	Austria ON
Flash point (℃)	212	129	76	130	120	110	100
Cloud point (℃)	18	9	−13	–	–	–	–
Pour point (℃)	14	5	−20	–	–	–	–
Calorific Value (kJ/kg)	35614	36914	42960	–	–	–	–
Kinematic Viscosity at 40℃ (cSt)	27.63	4.85	2.68	1.9−6.0	3.5−5.0	3.5−5.0	3.5−5.0
Density at 15℃ (kg/m^3)	915	883	846	–	860−900	875−890	850−890
Cetane Number	–	51	48	>47	>51	>49	>49

3.2 Effect of storage period

3.2.1 Effect of storage period on viscosity

Figure 3 shows the effect of storage period on viscosity of the biodiesel. It is clear from figure that the viscosity of biodiesel followed an increasing trend throughout the storage period of one year. During initial stages in the oxidation of fatty derivatives, primary products such as hydroperoxides increase in concentration, causing peroxide value to increase. These stages are defined collectively as the induction period. Following the induction period, decomposition of the hydroperoxides yields a mixture of secondary products including short chain carboxylic acids, ketones, epoxides, and mono- and dihydroxy compounds[15]. Once the induction period has passed and secondary degradation causes formation of soluble polymers, these polymers will tend to cause viscosity to increase.

The viscosity of MOB remained below the maximum viscosity value of 5 cSt up to storage period of 30 day. As such, to keep the viscosity within permissible limits as per fuel standards, the MO biodiesel should not be stored beyond 30 day.

3.2.2 Effect of storage period on acid value

The effect of storage period on acid value of the biodiesel is shown in Fig. 4. From the figure, it is observed that the acid value of the biodiesel increase with the increase in storage period. This is because the esters were first oxidized to form peroxides. Once fatty oil hydroperoxides are formed, they decompose to ultimately form aldehydes such as hexenals, heptenals, propanal, pentane and 2,4-heptadienal. One study detected about 25 aldehydes during the oxidation of vegetable oils. Aliphatic alcohols, formic acid and formate esters have also been detected. Increased acidity is always a result of oxidation of fatty oils and biodiesel, due to the formation of shorter chain fatty acids[16].

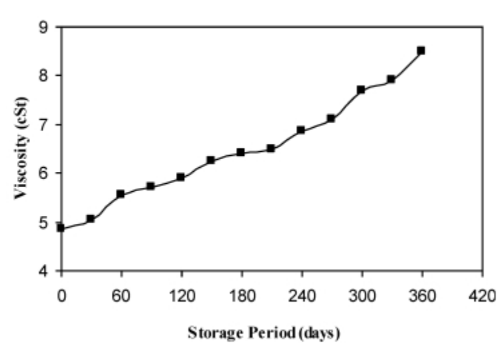

Fig. 3 Viscosity Vs Storage Period.

3.3 Effect of storage period on density

Figure 5 shows the variation of density of biodiesel during the storage period. The density of the biodiesel increased during storage. The fatty acid composition of MO is composed of 50-65 wt%, total unsaturated esters and has a relatively high degree of polyunsaturation. Unsaturated compounds are significantly more reactive to oxidation than saturated compounds; increasing the degree of unsaturation further increases reactivity[15]. The methylene groups adjacent to the double bonds are particularly susceptible to free radical attack. This attack occurs near double bonds. One consequence of the attack is production of short chain fatty acids from the oxidation products, which causes the acid value to increase. Some of the oxidation products may polymerize forming insoluble, high molecular weight sediments. The production of these sediments and the short chain acids may cause changes in the fuel density[17].

3.4 Effect of storage period on iodine value

The iodine value is a structure related index in chemistry that relates to the total number of double bonds in a fat or oil. Figure 6 shows the variation of iodine value of biodiesel during the storage period. The iodine value of the MOB decreased during storage.

In oxidative instability, the methylene carbons between the olefinic carbons are the sites of first attack. After hydrogen is removed from such carbons, oxygen rapidly attacks and a hydroperoxide is ultimately formed where the polyunsaturation has been isomerized to include a conjugated diene. This reaction is a chain mechanism that can

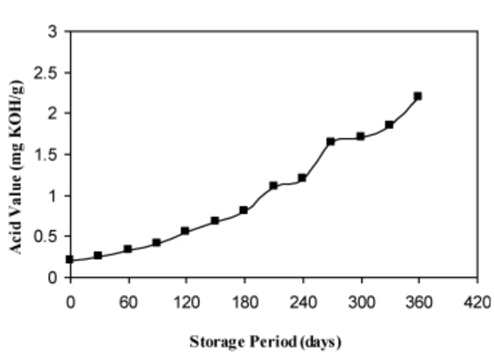

Fig. 4 Acid Value Vs Storage Period.

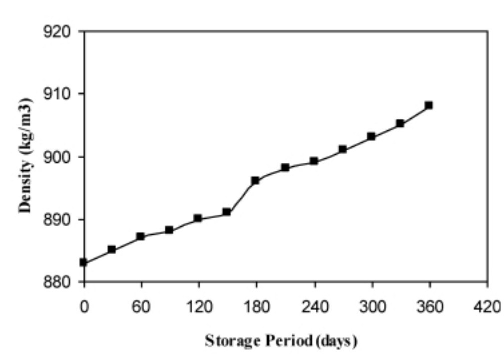

Fig. 5 Density Vs Storage Period.

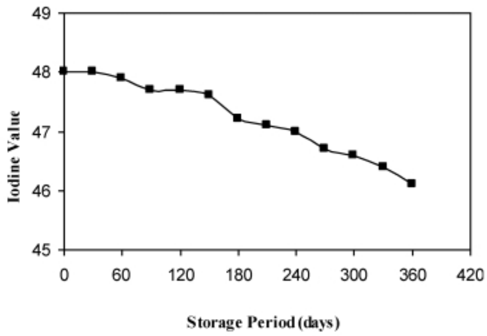

Fig. 6 Iodine Value Vs Storage Period.

proceed rapidly once an initial induction period has occurred. The greater the level of unsaturation in a fatty oil or ester, the more susceptible it will be to oxidation. Once the hydroperoxides have formed, they decompose and inter-react to form numerous secondary oxidation products including aldehydes, alcohols, shorter chain carboxylic acids, and higher molecular weight oligomers often called polymers. Another polymerization mechanism, vinyl polymerization, has been proposed as being part of the degradation process of fatty oils and esters[16]. Hence the Iodine value decreases with the storage period[18-20].

4 CONCLUSION

The properties of the MOB were found to be within the biodiesel limits of various countries. Hence the MOB can be used as a substitute for diesel, for sustainable development of rural areas and as a renewable fuel. It could be concluded from the storage study of biodiesel that viscosity, density and acid value showed an increasing trend during storage. The acid value of the biodiesel increased very rapidly during storage. Increase in density was observed to be marginal during the storage period. The viscosity of biodiesel remained below the maximum 5 cSt up to storage period of 30 day. As such, to keep the viscosity within permissible limits as per fuel standards of many countries, the MOB should not be stored beyond 30 day. Similarly, to take care of acid value permissible limits as per fuel standards, MOB should not be stored beyond 30 day. Combining these two, the MOB should not be stored beyond 30 day. From the experimental results, it is concluded that the biodiesel derived from non-edible MO looks to be a better alternative to diesel oil in India.

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