Storage Studies on Plant Oil Based Bio-Diesel Fuels

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ABSTRACT

Bio-diesel was prepared from three different oils namely Rice bran oil, *Jatropha curcas* oil and *Karanja* (*Pongamia pinnata*) oil. These were stored for one year to find out if there was any change in their quality during storage. Viscosity, free fatty acid content, and density were taken as quality parameters. All the three parameters showed an increasing trend during the storage period. This trend was observed in washed as well as unwashed bio-diesel of all the three oils studied.

Keywords: Bio-diesel, storage, rice bran oil, *Jatropha curcas* oil, *Karanja* oil, methyl ester, India.

1. INTRODUCTION

Modern agriculture depends heavily on petroleum based fuels especially diesel fuel. Known reserves of petroleum are limited. These are bound to get exhausted in not too distant a future. The threat of impending depletion of petroleum based fuels has led the scientists world over to search for alternate fuels especially fuels from renewable sources. Agricultural scientists are more interested in developing some biomass-based fuels as alternate fuels for diesel engines. Some of such fuels tried include plant oils (Shyam, 1984 and Romano, 1982), bio-gas (Das and Prasad, 1978), producer gas (Jain, 1987), and alcohol (Bandel, 1977) etc. Among these alternate fuels, plant oil-based fuels are considered to have a number of advantages over the others.

Use of plant oils as diesel engine fuel dates back to 1900, when Rudolf Diesel used peanut oil as fuel for compression ignition engines (Borgett et al., 1994). Diesel engines can be and have been run successfully on plant oils. But during long-term operation of the engine on plant oils, several problems (including excessive carbon deposition on engine parts) have been reported. Viscosity is considered to be the major reason for these problems. The promising method to overcome these problems is trans-esterification of plant oils. It gives a new product called bio-diesel (Gupta, 1994).

Plant oils are inherently less stable than diesel due to high degree of unsaturation of the plant oils. This unsaturation leads to gum formation during storage, which is due to oxidative polymerization (Korus et al., 1982). Presence of gum in a fuel causes hindrance in complete combustion resulting in carbon deposits in the combustion chamber and around the nozzle tips. The injection spray pattern is disrupted, the rings seize and the crankcase oil viscosity increases.

Although bio-diesels are expected to have a reduced tendency toward polymerization (Hasset and Hasan, 1982), studies were conducted to find out the effect of storage period on change in quality of bio-diesel.

2. MATERIALS AND METHODS

Plant oils namely Rice bran oil, *Jatropha curcas* oil, and *Karanja* oil were selected for the study. *Jatropha curcas* and *Karanja* oils were selected due to their non-edible nature. Rice bran oil was preferred because it was obtained from rice bran, a by-product of the rice processing industry, and is available throughout the year.

2.1 Preparation of Bio-Diesel

The bio-diesel was prepared using the method standardized by Gupta (1994). Each oil sample was heated up to 60° C. The required volume of alkaline methanol (homogeneous solution of 200 ml methanol and 10g NaOH for each litre of oil) was mixed with the heated oil and the mixture was stirred for 5-7 minutes. It was then kept undisturbed for 4 hours to allow the glycerol to settle at the bottom. The bio-diesel thus formed was called unwashed bio-diesel and was decanted from top leaving glycerol at the bottom. The unwashed bio-diesel was given 2 - 3 washings with water to remove the traces of glycerol, left over sodium catalyst, and other impurities present in it. Each time, water settled at the bottom within 5 minutes and the bio-diesel was decanted from top. In the end, the bio-diesel was heated to remove moisture left in it. This bio-diesel was called the washed bio-diesel.

2.2 Parameters Studied

During trans-esterification process, about 100% excess methanol (i.e. 100% more than the theoretical amount required for the process) is mixed with oil. As such, excess methanol remains unreacted and is present in the unwashed bio-diesel. During washing of bio-diesel, this excess methanol goes with water and is a loss. It can be saved either by recycling the excess methanol or by not washing the bio-diesel. Therefore, apart from washed bio-diesels, unwashed bio-diesels of all the three plant oils were also included in the study.

Viscosity of bio-diesel fuel is stated to be a fundamental property is the root cause of many problems associated with its use as fuel in the CI engine. High viscosity results in increased droplet size during injection of fuel into the cylinder and results in poor combustion (Kusy, 1982). Therefore, viscosity was considered as one of the indices for bio-diesel quality.

At elevated temperatures in the engine combustion chamber, the free fatty acids may react with metal parts forming fatty acid metal salts. These salts can lead to engine wear (Pryde, 1982). As such, free fatty acid (FFA) content of the bio-diesel was taken as a parameter.

Density of the bio-diesel was included as it will affect the bio-diesel mass flow per stroke of the injection pump plunger and, hence, will affect the power output of the engine. Also, the specific gravity of fuels is used as a precursor for a number of other fuel properties, such as heating value, viscosity and cetane number (Yuan et al, 2004).

As explained above, the washed as well as unwashed bio-diesels were stored in plastic containers for one year. The effect of storage period on the quality of bio-diesels was studied. Three bio-diesel parameters namely viscosity, free fatty acid content, and density were taken as quality indicators. The observations were recorded every month.

2.3 Measurement of Fuel Properties

Methods used to determine the selected properties of bio-diesels are discussed below:

2.3.1 Kinematic Viscosity

Kinematic viscosity of samples was measured with the help of Red Wood Viscometer No. 1 (Toshniwal make). Time of gravity flow of fixed volume (50 ml) of sample was measured. The experiment was performed at 38° C. Kinematic viscosity was calculated using the following formulae (BIS, 1976):

$$V_k = 0.24t - 50/t \qquad \text{for } t > 100$$

$$V_k = 0.26 - 179/t \qquad \text{for } 34 < t > 100$$

where V_k - Kinematic viscosity, cS
t - time of flow, s

2.3.2 Free Fatty Acid (FFA)

A known amount of sample was titrated with aqueous solution of NaOH of known normality. Per cent FFA was calculated using standard method (McKillican, 1966) as follows:

$$\%\ FFA = (VNM)/10w$$

where V - Volume of NaOH used, ml
N - Normality of NaOH
M - Molecular weight of fatty acid
w - weight of sample, g

2.3.3 Density

Density was measured using the standard method (BIS, 1972). Capillary stopper relative density bottles of 50 ml capacity were used to determine density of the bio-diesels. Relative density bottle was dried and weighed. Then sample was filled in the bottle and capillary stopper was placed gently on the neck of the bottle, taking care that no air bubble was left inside the bottle. Bottle was cleaned from outside with filter paper and then it was placed in an oven at 21° C. After few minutes, the bottle was taken out and cleaned from outside. Bottle was again kept in the oven to regain the temperature. Then, it was taken out and weighed. Density was calculated using the following equation:

$$d = (M_2 - M_1) / 50$$

where d - Density of the sample, g/ml
M_1 - Mass of empty relative density bottle, g
M_2 - Mass of relative density bottle plus sample, g

3. RESULTS AND DISCUSSION

The results of the storage study are presented and discussed here under different sub-heads as given below.

3.1 Effect of Storage Period on Viscosity of Bio-Diesels

Results for effect of storage period on viscosity of bio-diesels have been presented in Figures 1 and 2. The viscosity variation among different bio-diesels could be attributed to the structural variations (variations in the fatty acid compositions) of the bio-diesels.

It is clear from Figures 1 and 2 that the viscosity of bio-diesels (washed as well as unwashed) followed an increasing trend throughout the storage period of one year. The increase in viscosity of bio-diesels during storage was also reported by Verma et al. (1998).

The increase in viscosity during storage may be due to polymerization or partial oxidation. The more the unsaturation, the more is the polymerization (Lipinsky et al., 1982).

As expected, unwashed bio-diesels were having lower viscosity than that of their respective washed bio-diesels due to presence of excess methanol in the unwashed bio-diesels. However, the viscosity of unwashed *Karanja* bio-diesel became higher than that of its washed bio-diesel after a storage period of 90 days. This was because of very high increase in the viscosity of unwashed *Karanja* bio-diesel during the storage period.

All the washed as well as unwashed bio-diesels showed the viscosity more than the minimum BIS (Bureau of Indian Standard) recommended value of 2.0 cS. However, washed and unwashed Rice bran bio-diesel crossed the maximum BIS recommended value (7.5 cS) after 30 days and 90 days, respectively. Viscosity of washed and unwashed *Jatropha curcas* bio-diesel was below the maximum viscosity as suggested by BIS up to 210 days and 270 days, respectively. Both washed as well as unwashed *Karanja* bio-diesels were having viscosity values below the maximum BIS recommended value of viscosity (7.5 cS) up to 90 days of storage.

Percent increase in viscosity was also calculated and is given in Table 1. It is clear from Table 1 that the percent increase in viscosity was higher for unwashed bio-diesels compared to that of washed bio-diesels for all the three oils. The difference was more prominent in case of *Karanja* bio-diesels.

3.2 Effect of Storage Period on Free Fatty Acid (FFA) Content of Bio-Diesels

Figures 3 and 4 show that FFA of washed as well as unwashed bio-diesels increased during the storage period. The increase in FFA content of bio-diesels during storage has also been reported by Verma et al. (1998).

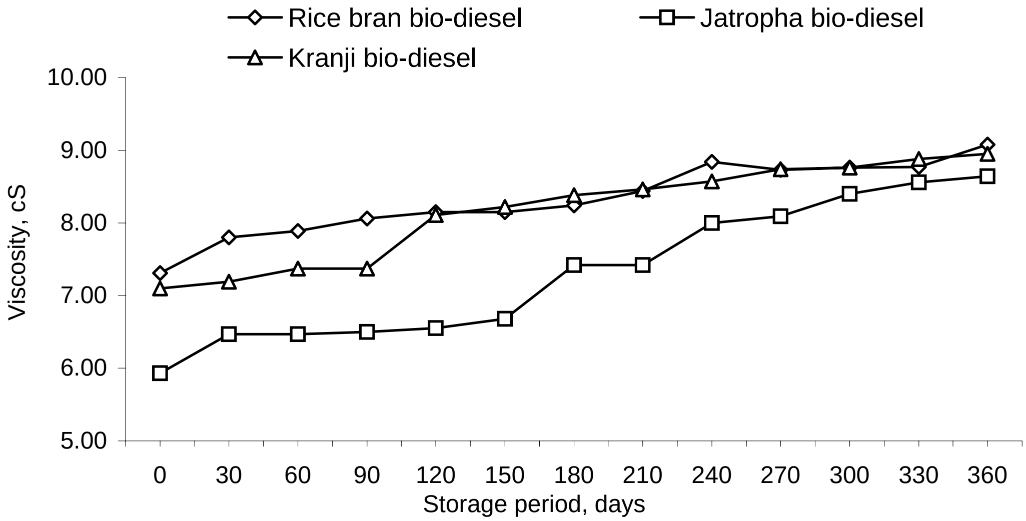

Figure 1. Effect of storage period on viscosity of washed bio-diesels.

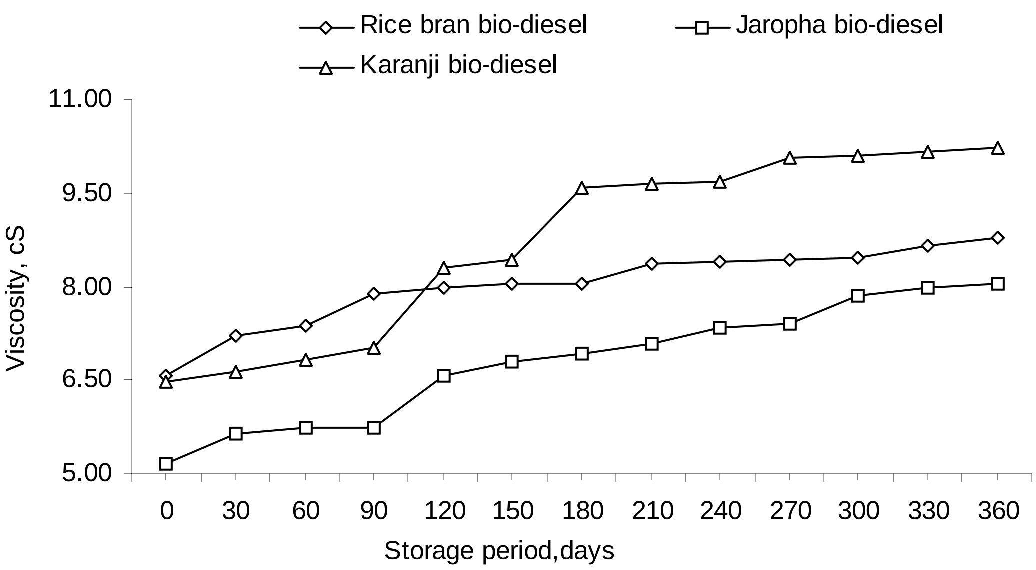

Figure 2. Effect of storage period on viscosity of unwashed bio-diesels.

Table 1. Percent increase in viscosity of washed and unwashed bio-diesels with storage period

Storage Period, days	Rice bran bio-diesel		*Jatropha curcas* bio-diesel		*Karanja* bio-diesel	
	Washed	Unwashed	Washed	Unwashed	Washed	Unwashed
0	-	-	-	-	-	-
30	6.7	9.8	9.1	9.1	1.3	2.8
60	7.9	12.3	9.1	11.0	3.8	5.7
90	10.3	20.4	9.6	11.2	3.8	8.3
120	11.5	21.6	10.5	27.3	14.2	28.1
150	11.5	22.9	12.6	31.3	15.8	30.1
180	12.7	22.9	25.1	34.2	18.0	48.1
210	15.5	27.6	25.1	37.1	19.2	49.0
240	19.3	27.9	34.9	41.8	20.7	49.8
270	19.4	28.4	36.4	43.3	23.1	55.8
300	19.8	29.1	41.7	51.6	23.4	56.0
330	20.0	32.2	44.4	54.4	25.1	57.3
360	24.2	34.1	45.7	55.9	26.1	58.3

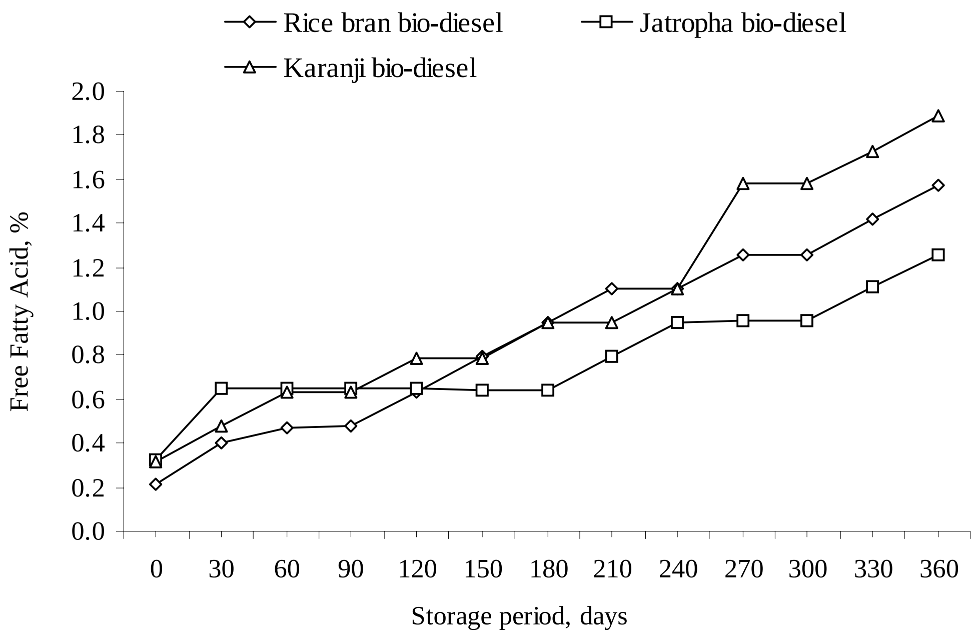

Figure 3. Effect of storage period on free fatty acid of washed bio-diesels.

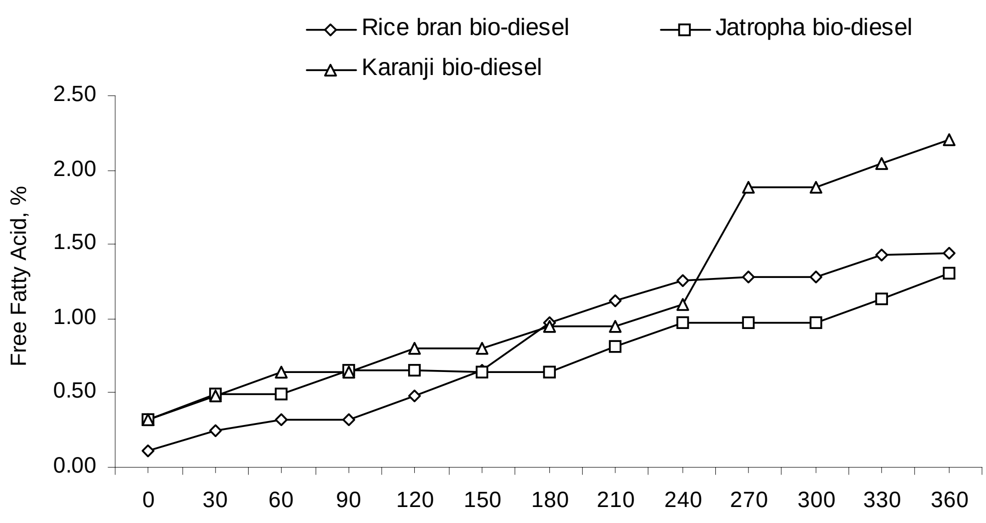

Figure 4. Effect of storage period on free fatty acid of unwashed bio-diesels.

Initial FFA content of washed Rice bran bio-diesel was higher than that of its unwashed bio-diesel but washed *Karanja* and *Jatropha curcas* bio-diesels were having almost same initial FFA as their respective unwashed bio-diesels had. The difference in FFA content of washed and unwashed *Jatropha curcas* bio-diesels remained almost same throughout the storage period. Washed and unwashed *Karanja* bio-diesels were having almost same FFA up to 240 days of storage but later on, the unwashed bio-diesel had higher increase in FFA.

The increase in FFA content may be attributed to hydrolytic oxidation due to high relative humidity. The FFA value of washed Rice bran bio-diesel was below the BIS recommended value of 0.5 up to 90 days of storage and that of unwashed Rice bran bio-diesel crossed the value after 120 days. In case of washed *Jatropha curcas* the limiting value was crossed before 30 days while FFA of unwashed *Jatropha curcas* bio-diesel was below up to 60 days. Both washed and unwashed *Karanja* bio-diesels crossed the BIS recommended value of FFA after 30 days.

Percent increase in FFA content was also determined and is given in Table 2. It is clear from the table that FFA content increased at very fast rate in case of Rice bran bio-diesels, which is due to inherent lipase activity. In general increase in FFA content of unwashed bio-diesel was higher compared to that in the washed bio-diesel for all three oils.

3.3 Effect of Storage Period on Density of Bio-Diesels

Figures 5 and 6 show that density of washed and unwashed bio-diesels increased during the storage period. Verma et al. (1998) also reported increase in density of bio-diesels during storage.

The increase in density during storage may be due to moisture absorption and reaction with air. All the washed bio-diesels were having little higher densities than their respective unwashed bio-diesels at the start of experiment. Among the washed bio-diesels, the *Karanja* bio-diesel was found to be denser followed by rice bran and *Jatropha curcas* bio-diesels. Percent increase in density was also calculated and is given in Table 3. It is clear that percent increase in density was quite low. Maximum value was 3.3 % increase.

4. CONCLUSIONS

It could be concluded from the storage study of bio-diesels that all the three parameters selected (viscosity, density and free fatty acid) for study showed an increasing trend during storage. FFA content increased very rapidly during storage particularly in case of Rice bran bio-diesels. Increase in density was observed to be marginal in all the stored bio-diesels.

The viscosity of washed Rice bran bio-diesel, *Karanja* bio-diesel, and *Jatropha curcas* bio-diesel remained below the maximum BIS value of 7.5 cS up to storage period of 30, 90, and 210 days respectively. As such, to keep the viscosity within permissible limits as per BIS recommendations, Rice bran bio-diesel, *Karanja* bio-diesel and *Jatropha curcas* bio-diesel should not be stored beyond 30, 90, and 210 days respectively. Similarly, to take care of FFA content in regard to permissible limits as per BIS recommendations, Rice bran bio-diesel, *Karanja* bio-diesel and *Jatropha curcas* bio-diesel should not be stored beyond 90, 30, and 30 days respectively. Combining the two, all the three bio-diesels should not be stored beyond 30 days.

Table 2. Percent increase in Free Fatty Acid (FFA) content of washed and unwashed bio-diesels with storage period

Storage Period, days	Rice bran bio-diesel		*Jatropha curcas* bio-diesel		*Karanja* bio-diesel	
	Washed	Unwashed	Washed	Unwashed	Washed	Unwashed
0	-	-	-	-	-	
30	90.5	120.9	100.0	49.8	50.0	50.2
60	123.8	194.5	100.0	49.8	100.0	100.0
90	126.2	194.5	99.7	99.1	100.0	98.5
120	201.9	336.4	99.7	99.1	148.4	147.7
150	276.7	488.2	97.5	96.9	148.4	147.7
180	351.9	779.1	97.5	96.9	198.7	194.1
210	426.7	918.2	145.7	148.3	199.1	195.4
240	426.7	1045.5	193.2	198.5	245.9	240.6
270	500.0	1063.6	194.8	198.5	396.9	485.1
300	500.0	1063.6	194.8	198.5	396.9	482.0
330	576.2	1200.0	242.6	247.7	444.0	531.6
360	647.6	1209.1	288.9	300.0	494.3	581.1

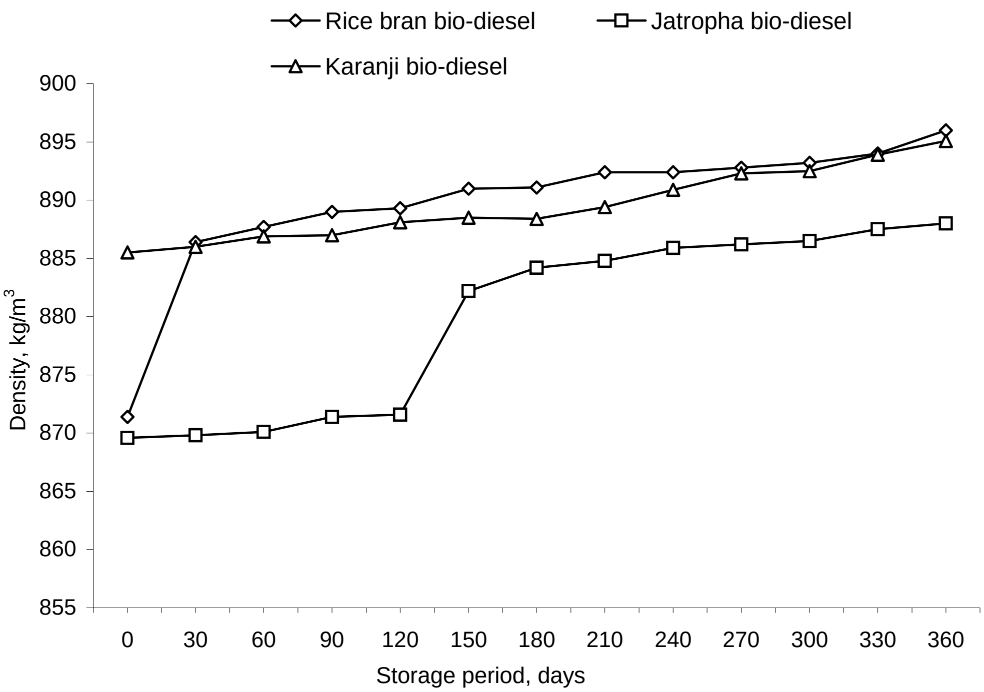

Figure 5. Effect of storage period on density of washed bio-diesels.

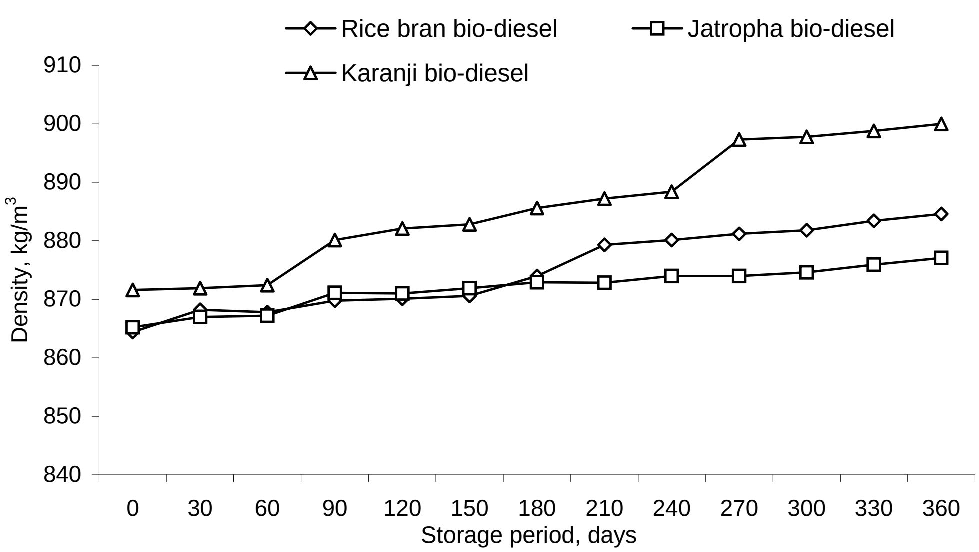

Figure 6. Effect of storage period on density of unwashed bio-diesels.

Table 3. Percent increase in density of washed and unwashed bio-diesels with storage period

Storage Period, days	Rice bran bio-diesel		*Jatropha curcas* bio-diesel		*Karanja* bio-diesel	
	Washed	Unwashed	Washed	Unwashed	Washed	Unwashed
0	-	-	-	-	-	-
30	1.7	0.4	0.0	0.2	0.1	0.0
60	1.9	0.4	0.1	0.2	0.2	0.1
90	2.0	0.6	0.2	0.7	0.2	1.0
120	2.1	0.7	0.2	0.7	0.3	1.2
150	2.2	0.7	1.4	0.8	0.3	1.3
180	2.3	1.1	1.7	0.9	0.3	1.6
210	2.4	1.7	1.7	0.9	0.4	1.8
240	2.4	1.8	1.9	1.0	0.6	1.9
270	2.5	1.9	1.9	1.0	0.8	2.9
300	2.5	2.0	1.9	1.1	0.8	3.0
330	2.6	2.2	2.1	1.2	0.9	3.1
360	2.8	2.3	2.1	1.4	1.1	3.3

It is suggested that more detailed study should be conducted taking a large number of samples of each bio-diesel. Studies should also be carried out to see the effect, if any, of initial environmental temperature (i.e the weather conditions at the start of the experiment).

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