TECHNICAL ASPECTS OF BIODIESEL PRODUCTION FROM VEGETABLE OILS

by

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Original scientific paper
UDC: 665.3:543.632.514.3
BIBLID: 0354-9836, *12* (2008), 2, 159-169
DOI: 10.2298/TSCI0802159K

Biodiesel, a promising substitute as an alternative fuel has gained significant attention due to the finite nature of fossil energy sources and does not produce sulfur oxides and minimize the soot particulate in comparison with the existing one from petroleum diesel. The utilization of liquid fuels such as biodiesel produced from vegetable oil by transesterification process represents one of the most promising options for the use of conventional fossil fuels.

In the first step of this experimental research, edible rice bran oil used as test material and converted into methyl ester and non-edible jatropha vegetable oil is converted into jatropha oil methyl ester, which are known as biodiesel and they are prepared in the presence of homogeneous acid catalyst and optimized their operating parameters like reaction temperature, quantity of alcohol and the catalyst requirement, stirring rate and time of esterification. In the second step, the physical properties such as density, flash point, kinematic viscosity, cloud point, and pour point were found out for the above vegetable oils and their methyl esters. The same characteristics study was also carried out for the diesel fuel for obtaining the baseline data for analysis. The values obtained from the rice bran oil methyl ester and jatropha oil methyl ester are closely matched with the values of conventional diesel and it can be used in the existing diesel engine without any hardware modification. In the third step the storage characteristics of biodiesel are also studied.

Key words: *rice bran oil methyl ester, jatropha methyl ester, esterification, optimization, properties, storage*

Introduction

Biodiesel is an alternative fuel made from renewable biological resources such as vegetable oils (both edible and non edible oil) and animal fats [1, 2].

Vegetable oils are usually triesters of glycerol with different chain length and degree of saturation. The typical molecular structure of vegetable oil is shown in fig. 1. It may be seen that vegetable oils contain a substantial amount of O_2 in their molecules.

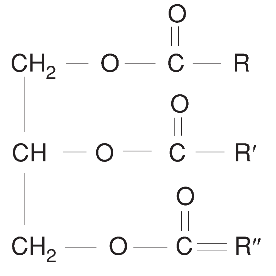

Figure 1. Typical structure of vegetable oil

Where R, R , and R are parts of the higher fatty acids forming ester with glycerol.

In 1911, Rudolf Diesel, discovered the diesel engine made a statement that it is generally forgotten that vegetable and animal oils can be directly used in diesel engine. Practically the high viscosity of vegetable oils (30-200 Cst) as compared to diesel oil (5.8-6.4 Cst) leads to unfavorable pumping, inefficient mixing of fuel with air contributes to incomplete combustion, high flash point result in increased carbon deposit formation and injector coking. Because of these problems, vegetable oils need to be modified to bring their combustion related properties closer to those of mineral diesel oil. The fuel modification is mainly aimed at reducing the viscosity and increasing the volatility.

One of the most promising processes to convert vegetable oil into methyl ester (bio diesel) is the transesterification, in which alcohol reacts with triglycerides of fatty acids (vegetable oil) in the presence of catalyst [3]. This paper briefly describes about the biodiesel production, optimization of process parameters, characterization and storage of biodiesel from rice bran oil and jatropha vegetable oil.

Material and methods

Material

Paddy is the important crop cultivated in India. With the locally available paddy, the rice bran to the tune of around 20,000 tonnes could be available even at conservative rate of 6% of paddy hulled. This surplus bran available locally can be utilized for extraction of oil. At present, India is the largest producer of edible grade rice bran oil with 27,000 tonnes per annum against the potential of 7.5 lakhs tonnes. Similarly India has rich and abundant forest resources with a wide range of plants and oil seeds. Jatropha vegetable oil is one of the prime non edible oil sources available in India. These two available sources are used for the production of bio diesel.

The physical and chemical properties of rice bran oil and jatropha oil is given in tab.1

Methods

Different methodologies used for the production of bio diesel are blending, micro emulsion, pyrolysis, and transesterification. From various studies, it is found that transesterification is the best way to modify the vegetable oil to be compatible diesel engine fuel. The transesterification is further classified into catalytic transesterification, super critical transesterification and non catalytic super critical transesterification. Catalytic transesterification is the current method of choice in this study.

Transesterification is a common and well established chemical reaction in which alcohol reacts with triglycerides of fatty acids (vegetable oil) in the presence of catalyst. It is a reversible reaction of fat oil (triglycerides) with a primary alcohol to form esters and glycerol [4]. The transesterification reaction is shown in fig. 2. A catalyst is usually used to improve the reaction rate and yield.

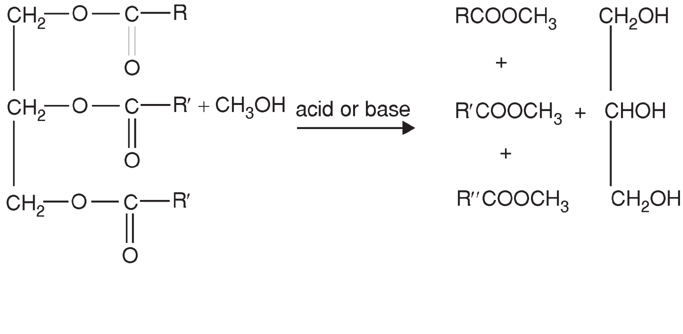

Figure. 2. Transesterification reaction of vegetable oil

Table.1. Physical and chemical properties of rice bran oil and jatropha oil

Properties	Rice bran oil	Jatropha oil
Colour	Brownish	Yellowish orange
Odour	Agreeable	Disagreeable
Taste	Pleasant	Bitter
Acid value	Not detected	38.12
Saponification value	187.5	194.8
Iodine value	102.6	101.8
Viscosity (Cst) at 40 °C	43.02	41.2
Palmitic acid	Not detected	4.3%
Stearic acid	Not detected	6.8%
Oleic acid	Not detected	50.4%
Linoleic acid	Not detected	34.8%
Other acids	Not detected	3.7%
Flash point [°C]	310	214
Fire point [°C]	340	256
Cloud point [°C]	14	11
Pour point [°C]	2	6

Since transesterification reaction is an equilibrium reaction, where more amount of alcohol is required to shift the reaction equilibrium to right side and produced more esters as proposed product [5]. Methanol and ethanol are used most frequently; especially methanol is preferred because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides and NaOH gets easily dissolved in it. Ethyl ester and methyl ester almost has same heat content. Viscosity of ethyl ester is slightly higher and pour point is slightly lower than those of methyl ester.

Experimental procedure

Neutralization

The vegetable oil used for biodiesel production might contain free fatty acids, which will enhance saponification reaction as side reaction during the transesterification process. This will reduce the conversion of vegetable oil into biodiesel and also leads to the formation of soap, causing difficulties in the separation of biodiesel and glycerin [6].

The vegetable oils contain about 14-19.5% of free fatty acids in nature, it must be freed before taken into actual conversion process. The presence of about 14% of free fatty acid makes the oil inappropriate for industrial biodiesel production.

The dehydrated oil is agitated with 4% HCl solution for 25 minutes and adds 0.82 g of NaOH per 100 ml of oil to neutralize the free fatty acid and is coagulated by the following reaction:

$$\mathrm{RCOOH + NaOH} \qquad \mathrm{RCOONa + H_2O}$$

The coagulated free fatty acid (soap) is removed by filtration. This process brings the free fatty acid content to below 0.5% [7] and is a perfect source (96-99% conversion achievable) for bio diesel production.

Biodiesel production

In this study, the base catalyzed transesterification is selected as the process to make biodiesel from jatropha oil. Transesterification reaction is carried out in a batch reactor. The reactor has three openings; in that one is at centre and another two are at the side. A condenser is provided at the centre to reduce the loss of solvent by evaporation and to maintain the pressure in the reactor. One of the side openings is used to provide thermometer, which helps to monitor the temperature of the reaction and the other one is used to pour the reactants. The reactor is placed on the hot plate with magnetic stirrer to heat and stir the reactant mixture [8-10].

For transesterification process, 500 ml of rice bran oil and 500 ml of jatropha oil is heated up to 70 ºC in two separate round bottom flasks to drive off the moisture and stirred vigorously. Methanol of 99.5% purity, having density 0.791 g/cm^3 is used. 2.5g of catalyst NaOH for rice bran oil and 5 g of catalyst NaOH for jatropha oil is dissolved in methanol, in 6:1 molar ratio, in a separate vessel and was poured into round bottom flasks while stirring the mixture continuously. Both the mixture was maintained at atmospheric pressure and 60 ºC for 60 minutes [8, 11, 12].

After completion of transesterification process, the product mixtures were allowed to settle under gravity for 24 hours in two separating funnels. The products formed during transesterification were rice bran oil methyl ester (ROME) and glycerol, jatropha oil methyl ester (JOME) and glycerin. The bottom layer consists of glycerin, excess alcohol, catalyst, impurities, and traces of unreacted oil. The evaporation of water and alcohol gives 80-88% pure glycerin, which can be sold as crude glycerin. For further purification, the crude glycerin is distilled by simple distillation.

The top layer consists of methyl ester, residual catalyst, methanol traces and other impurities. For washing and purification of methyl ester, it was mixed, washed with hot distilled water (10% v/v) at 70 °C to remove the unreacted alcohol, oil and catalyst are allowed to settle under gravity for 24 hours. Two layers were formed, the upper layer was the biodiesel and the lower layer was made of water and impurities. This process was repeated until the lower phase had a pH value that was similar to that of distilled water, thus indicating that only water was present and the catalyst is removed completely in the washing. It was found that during washing some ester was lost due to emulsion formation. The separated biodiesel is taken for characterization. The block diagram for the production of biodiesel is shown in fig. 3. The experimental setup for bio diesel production was shown in fig. 4.

Results and discussion

Additional experiments were conducted with NaOH as a catalyst to study the effect of different parameters like reaction temperature, molar ratio of alcohol to oil and amount of catalyst on the ester yield as well as the extent of conversion, which can be represented by the viscosity of ester. The stirring speed was kept constant at 500 rpm for all experiments.

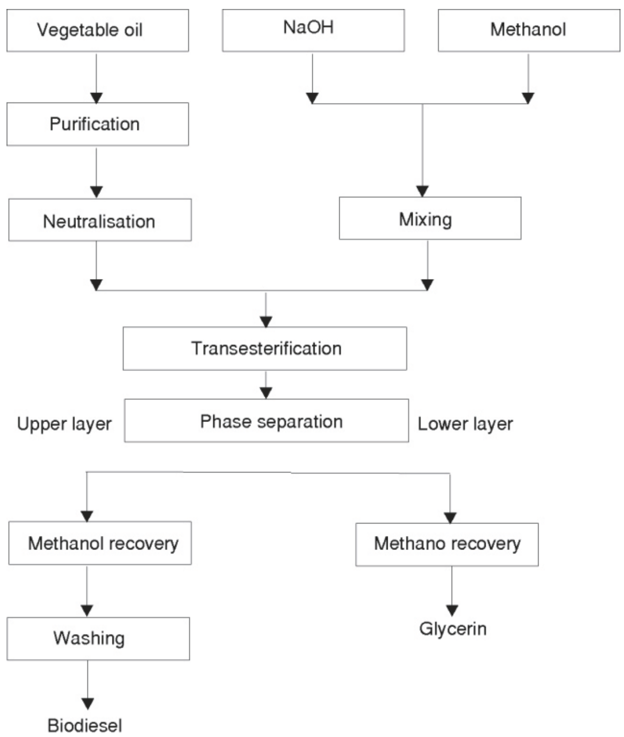

Figure 3. Block diagram for biodiesel production

Effect of reaction time

Several investigators found that reaction starts very fast and almost 80% of conversion takes place in first 5 minutes and after 1 hour almost 93-98% conversion of triglycerides into ester takes place. In present work, effect of reaction time from 45 minutes to 120 minutes on the methyl ester (biodiesel) yield from rice bran oil and jatropha oil and their corresponding effect on viscosity were observed. From the observation it was found that ester yield increased as the reaction time increases. However if the reaction time was increased beyond 1 hour, the ester yield was decreased for rice bran oil and slightly increased for jatropha oil. But there was no significant effect on the viscosity of the ester obtained from the vegetable oils was shown in the figs. 5 and 6.

Effect of reactant ratio

One of the important parameter affecting the yield of the ester is the molar ratio of alcohol to vegetable oil employed. The stoichiometric requirement for transesterification was 3:1 to yield 3 mole of ester and one mole of glycerin.

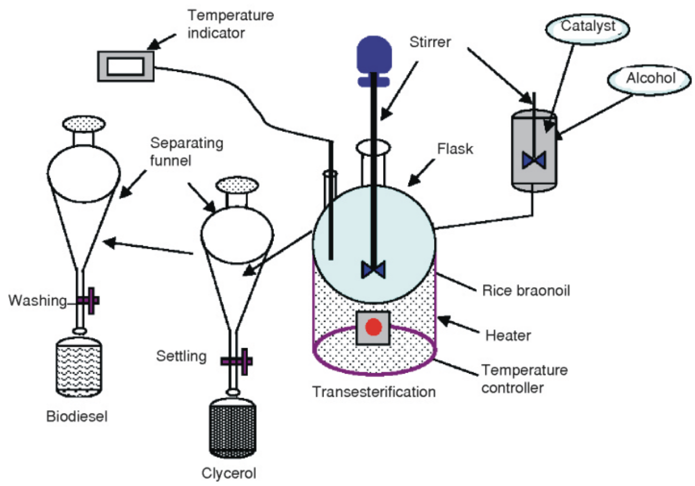

Figure 4. Experimental setup for biodiesel production

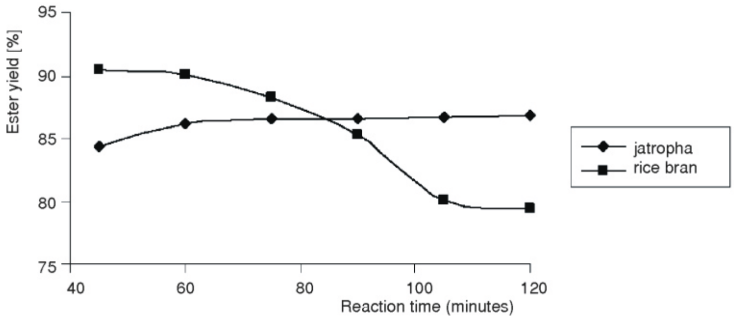

Figure 5. Effect of reaction time on ester (biodiesel) yield

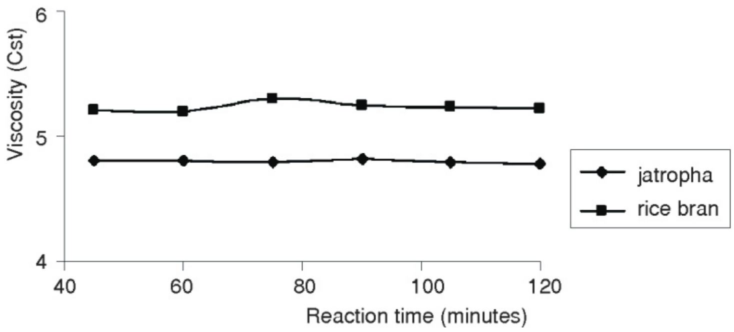

Figure 6. Effect of reaction time on viscosity

But most of the researchers found that excess alcohol was required to drive the reaction close to completion. The effect of methanol in the range of 4:1 to 11:1 (molar ratio) was studied and by keeping the other parameters fixed.

The optimum reactant ratio is around 6:1 moles of methanol per mole of rice bran oil and jatropha oil. It was found that ester yield increases with increase in molar ratio of methanol to vegetable oil but the incremental gain in ester yield decreases with increase in the molar ratio. When reactant is going on increasing the density difference between upper and lower layer (the two phases obtained after transesterification) keeps decreasing and hence leads to problems in separating the two. At higher reactant ratio a large amount of alcohol is present in the transesterified products, requires large amount of energy to distill the products. The results of this study were shown in fig. 7. But there is no significant difference in viscosity of the ester for both cases and is shown in fig. 8.

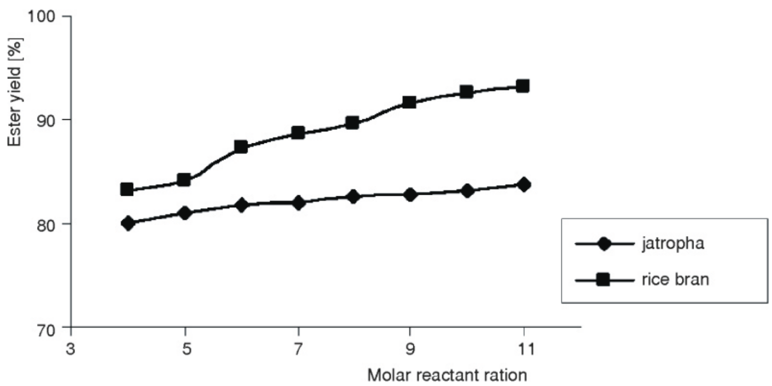

Figure 7. Effect of reactant time on biodiesel yield

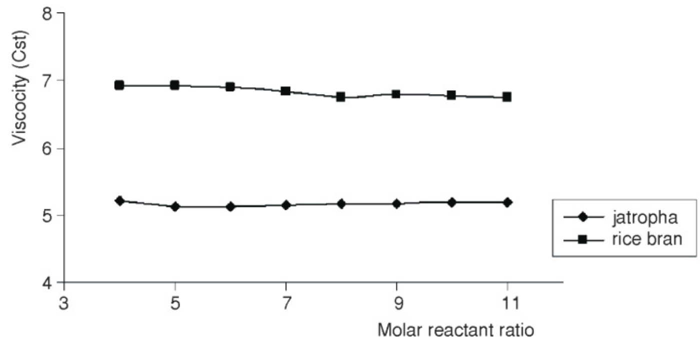

Figure 8. Effect of reactant ratio on viscosity

Effect of reaction temperature

Several researchers found that the temperature increase influence the reaction in a positive manner. Dorado *et al.* [13] found that ester yield slightly decreases above 50 °C reaction temperature. However other researchers found better results for higher temperature. For studying the effect of temperature on the transesterification reaction, the reaction temperature was performed at 45, 50, 55, 60, 65, and 70 °C while the other parameters were kept constant. The effect of reaction temperature on the biodiesel yield is shown in fig. 9. The temperature increase influences the ester yield in a positive manner till 55 °C for rice bran oil and after that it decreases. The temperature increase in the case of jatropha oil shows slight increase in ester yield till 60 °C after that it decreases. However reaction temperature of more than 60 °C should be avoided, because the ester yield decreased above 60 °C. It may be probably due to negative interaction between temperature and catalyst concentration, due to side reaction such as soap formation. Some researchers reported that reaction temperature more than 60 °C should be avoided because they tend to accelerate the saponification of the glycerides by the alkaline catalyst before completion of the alcoholysis [6, 8, 11]. The viscosity of rice bran oil methyl ester increases slightly as the reaction temperature increases, but notable increase in the viscosity of jatropha methyl ester was observed beyond 55 °C and is shown in fig.10

Effect of catalyst concentration

The effect of NaOH concentration was studied in the range of 0.5-1.5% (weight of NaOH/weight of oil), while the other parameters were kept constant. The catalyst concentration increase influences the ester yield in a positive manner up to 0.92% NaOH for jatropha oil after that it decreases. It was found that ester yield for rice bran oil decreases as the amount of catalyst

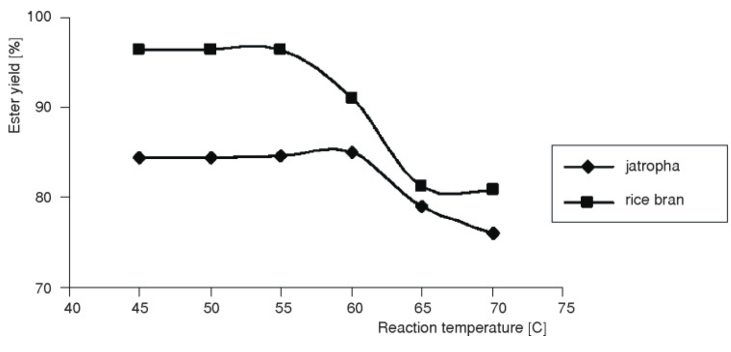

Figure 9. Effect of reaction temperature on biodiesel yield

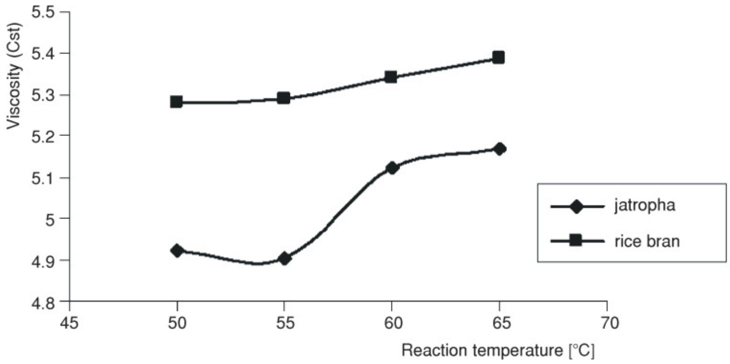

Figure 10. Effect of reaction temperature on viscosity

was increased from 0.5 to 1.5%. The ester yield decreases drastically as the NaOH concentration was increased above 1% and reduces to almost 50 for 1.5% NaOH concentration. For a concentration of 1.25%, both of the oil performs similarly and is shown in fig. 11.Viscosity decreases up to 0.92% NaOH concentration for jatropha methyl ester and viscosity decreases up to 0.75% for rice bran methyl ester and after that it is almost constant in both esters and are shown in fig. 12.

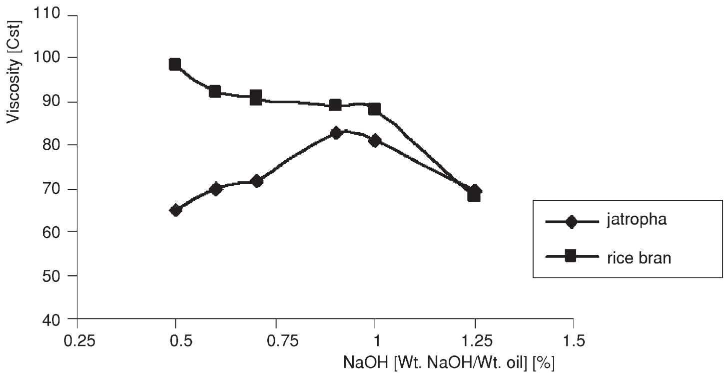

Figure 11. Effect of catalyst concentration on bio diesel yield

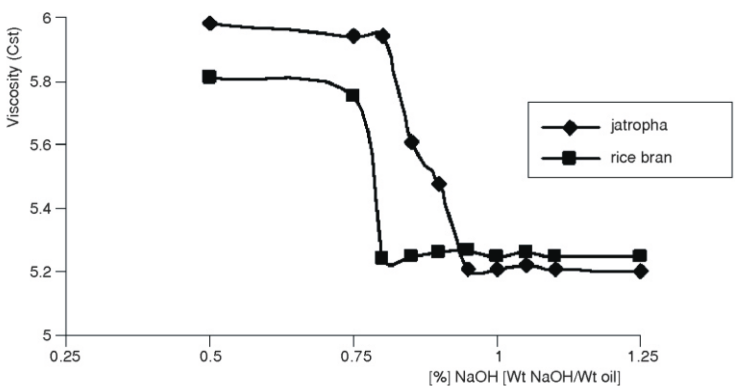

Figure 12. Effect of catalyst concentration on the viscosity

Biodiesel characterization

The fuel properties of the biodiesel from the jatropha oil and rice bran oil and diesel were determined through standard tests and equipments. The properties of the vegetable oils and their methyl esters and diesel values are given in tab. 2.

Table 2. Fuel properties of vegetable oils, esters, and diesel

Properties	Petroleum derived diesel	Jatropha vegetable oil	JOME	Rice bran oil	ROME
Flash point [°C]	65	214	128	316	183
Fire point [°C]	78	256	136	337	196
Pour point [°C]	– 6	6	–2	1	–2
Cloud point [°C]	5	11	8	13	9
Viscosity at 40 °C [Cst]	2.86	36.92	4.82	43.52	5.29
Viscosity index	98	181	154	Not detected	Not detected
Specific gravity (29 °C)	0.792	0.944	0.84	0.920	0.877
Refractive index at 40 °C	1.32	1.61	1.46	1.471	1.39
Calorific value [MJ/kg]	44.34	39.76	42.80	38.22	41.20

It can be seen from tab. 2 that the specific gravity of JOME and ROME is higher than that of diesel. It shows that specific gravity reduces after transesterification, viscosity reduces from 57 Cst to 4.82 Cst for jatropha oil and from 43.2 Cst to 5.29 Cst for rice bran oil, which is acceptable as per ASTM norms for biodiesel. This property is mainly important in airless combustion systems because it influences the efficiency of automation of the fuel [14, 15].The cloud and pour point of JOME was found 8 °C and –2 °C, respectively, which is higher than the diesel but lower than the values of jatropha vegetable oil. Similarly the cloud and pour point of ROME was found 9 °C and – 2 °C, respectively, which is higher than the diesel but lower than the values of rice bran oil.

Flash point and fire point are important temperature specified for safety during transport, storage, and handling. The flash point and fire point of JOME and ROME was found and decreases after transesterification when compared to original vegetable oils, which shows that its volatility characteristics had improved and it also safe to handle.

Storage of biodiesel

Bio diesel should be stored in clean dry tanks. Though the flash point of biodiesel is high, still some storage precautions are needed to be taken. It can be stored for long periods in closed containers with little head room but the container must be protected from direct sunlight, low temperature, and weather. Underground storage is preferred in cold climates, but low temperature can cause biodiesel to gel. The biodiesel or its blends should be stored at temperature of at least 15 °C higher than the pour point of the fuel. While blending the biodiesel care should be taken to avoid very low temperatures as the saturated compounds can crystallize and separate out to cause plugging of fuel lines and filters.

Biodiesel and its blends are susceptible to growing microbes when water is present in fuel. Contact or condensation of water in the tank should be avoided because hydrocarbon degrading bacteria and mold can grow and use bio diesel as food. Being a mild solvent biodiesel has the tendency to dissolve and form sediments if stored in old tanks and it cause filter blockage, injector failure in addition to clogging of fuel lines. Brass, copper, zinc, and other oxidizing metals can oxidizes the biodiesel and form sediments in the tank, results a colour change. Hence storage tank made of aluminum or steel should be used. Adequate data on the effect of long term storage on the stability of biodiesel and blends are not available. Based on the experience so far, it is recommended that biodiesel can be stored up to a maximum period of six months.

Conclusions

In the current investigation, it has enabled us to confirm that jatropha oil as well as rice bran oil may be used as a resource to obtain biodiesel. JOME and ROME has become more attractive to replace petroleum fuel. As per the literature study, most of the transesterification studies have been done on edible oils like rapeseed, soybean, sunflower, and canola by using methanol and NaOH /KOH as catalyst. Rice bran oil and jatropha oil is one of the most potential source to produce bio diesel in India, which could offer opportunities for generation of rural employment, increasing income and improving environment. The above experimental result reveals the alkaline catalyzed transesterification was a promising area of research for production of biodiesel in large scale.

Effect of different parameters such as temperature, time, reactant ratio and catalyst concentration on the bio diesel yield was analyzed. The best combination of the parameters was found as (1) 6:1 molar ratio of methanol to oil for both oils, (2) 0.92% sodium hydroxide catalyst for jatropha oil and 0.75% for rice bran oil, (3) 60 °C reaction temperature for both oils, and (4) 60 minutes of reaction time for both oils. The viscosity of jatropha oil and rice bran oil reduces substantially after transesterification and comparable to diesel.

Biodiesel is considered as clean fuel since it has almost no sulphur, no aromatic and has about 10% inbuilt O_2 which helps it to burn completely. Its higher cetane number improves the ignition quality even when blended in the petro-diesel. Biodiesel produces lower CO emission; it reduces CO emission of about 25% to that of diesel fuel.

Biodiesel (JOME and ROME) characteristics like density, viscosity, flash point, cloud, and pour point are within the specification of ASTM norms. Finally it is concluded that based on the field trails and storage, biodiesel from jatropha oil and rice bran oil could be recommended as a fuel, if engine performance tests provide satisfactory results.

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Paper submitted: January 20, 2008
Paper revised: January 21, 2008
Paper accepted: March 15, 2008