Production of Biodiesel from Karanja (*Pongamia pinnata*) Oil and Comparison of Its Fuel Properties with Commercial Diesel

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Abstract

The present study deals with the transesterification of Karanja (*Pongamia pinnata*) oil with methanol to check the feasibility of methanolysis process by using sodium hydroxide as a catalyst. The yield of karanja biodiesel was about 85% when transesterification was carried out using 9:1 molar ratio of oil/methanol and 1% (w/w) sodium hydroxide of the oil. The fuel properties like density, viscosity, flash point, cloud point, pour point, cetane number, ash content, carbon residue, sulfur content and acid value of karanja biodiesel was determined and compared with conventional diesel for assessing the fuel quality of karanja-based biodiesel.

Key words: Karanja oil, Biodiesel, Transesterification, Fuel Properties.

1. Introduction

Due to gradual depletion of world petroleum reserves and the impact of environmental pollution of increasing exhaust-emissions, there is an urgent need for suitable alternative fuels for use in diesel engines. In view of this, vegetable oil is a promising alternative because of its several advantages-it is renewable, environment-friendly and produced easily in rural areas, where there is an acute need for modern forms of energy [1-5]. Biodiesel is an alternative fuel similar to conventional or 'fossil' diesel, which can be directly produced from vegetable oil, animal oil/fats, tallow and waste cooking oil. Therefore, in recent years systematic efforts have been made by several research groups [6-9] to use vegetable oils as fuel in engines. Of course, the use of non-edible vegetable oils compared to edible one is very significant because of the tremendous demand for edible oils as food and they are far too expensive to be used as fuel at present. In this context, nonedible oil sources such as Jatropha curcas has been found as a potential source of biodiesel for most of the developing countries. Recently, one more plant species viz. Karanja (Pongamia pinnata), known as non-edible oil source has been investigated for biodiesel production [10]. Although neat vegetable oils occupy a prominent position in the development of alternative fuels, there have been many problems associated with using it directly in diesel engine to its high viscosity. To overcome the problems associated with the very high viscosity of neat vegetable mis, the oil is either cracked, blended with low viscosity solvents or converted to methyl esters through mansesterification. The latter one, the transesterification process is a significant method for the manufacture of modiesel from the corresponding vegetable oils, in batch or continuous systems, where one ester is converted into mother. This reaction proceeds with catalyst (base or acid) without catalyst by using primary or secondary monohydric aliphatic alcohols, where the glycerol based mesters (or triacyl glycerides) that make up the fats and oils are converted into monoesters yielding free glycerol as a

byproduct [11]. In the present study, we report the extraction of karanja oil from karanja seeds and its conversion to biodiesel through transesterification process and compared its fuel properties with commercial diesel.

2. Materials and Methods

Extraction of Karanja oil from Karanja seeds

Karanja seeds were purchased from the local market of Dhaka in October 2007 and the seeds were sun-dried for several days for better grinding. The dried seeds were then ground into coarse powder. About 500 gm of the coarse seed powder was successively extracted with *n*-hexane and petroleum ether in a Soxhlet apparatus at reflux temperatures of the corresponding solvents. The individual extractives were then filtered off through a cotton plug followed by cloth filter and filter paper. The volume of the combined filtrates was reduced using Buchii rotary evaporator at low pressure. The highly viscose and dark brown colored extract thus obtained was dried under vacuum and termed as karanja oil. which was directly used as main raw material for the production of biodiesel. The yield of karanja oil obtained was about 30% by weight and its fuel properties were determined (Table-2). The extraction experiment was repeated for two more times.

Transesterification

Transesterification or alcoholysis is a kind of organic reaction where an alcohol reacts with an ester to give another alcohol and ester. In transesterification of vegetable oil/fat, a triglyceride reacts with an alcohol to produce esters and glycerin. The reaction proceeds essentially by mixing the reactants, and a catalyst (strong acid or base) is used to accelerate the conversion and yield. However, alkali transesterification is faster and hence it is used commercially. Among the alcohols, methanol and ethanol are used commercially because of their low cost and their physical and chemical advantages. They quickly react with triglycerides and catalysts and are easily dissolved in them. To complete a transesterification process, 3:1 molar ratio of 26

oil to alcohol is usually needed. This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction has been represented by Scheme-1. In this study, the reaction was conducted in methanol in presence of a strong base catalyst, namely, NaOH. Scheme-2 represents the methanolysis of triglycerides.

 $\begin{array}{c} \text{RCOOR}^{1} + \text{R}^{2}\text{OH} & \overbrace{}^{\text{catalyst}} \text{RCOOR}^{2} + \text{R}^{1}\text{OH} \\ \\ \text{Ester} & \text{Alcohol} & \text{Ester} & \text{Alcohol} \end{array}$

Scheme-1 General equation of transesterification

$H_{2}C-OCOR^{1}$ $H_{2}C-OCOR^{2}$ $H_{2}C-OCOR^{3}$	÷	3 CH ₃ OH	catalyst acid/base	CH ₂ OH CHOH + CH ₂ OH	$R^{2}COOCH_{3}$ $R^{2}COOCH_{3}$ $R^{3}COOCH_{3}$
Vegetable oil (Triglyceride)		Methanol		Glycerol	Methyl esters

Scheme-2 General equation for methanolysis of triglycerides

3. Experimental

Preparation of Sodium Hydroxide-Methanol Solution

Methanol was distilled to remove moisture. The moisture free methanol was used to prepare sodium hydroxidemethanol solution. The alcohol-catalyst solution was prepared freshly in order to maintain the catalytic activity and to avoid moisture absorbance. The reaction was conducted at different catalytic concentrations of NaOH.

Process of Transesterification Reaction (General Procedure)

A 200 ml two-necked round-bottomed flask was used as a reactor. The flask was equipped with a condenser and placed in a water bath, whose temperature could be controlled within \pm 2 °C. To a known amount (100 g) of karanja oil, 1 g of catalyst (NaOH) in methanol and 11.2 g of methanol was added under stirring. After closing properly, the flask it was put on the water bath. The system was maintained airtight to avoid the loss of alcohol. The reaction mixture was maintained at temperature just above the boiling point of the methanol i.e. around 70 °C to speed up the reaction rate. A little excess of alcohol was used to ensure total conversion of the oil to its esters and the maximum conversion was found with 9:1 molar ratio of oil to methanol. The formation of karanja oil methyl ester was monitored by using thin layer chromatography (TLC) technique using 80:20 hexane/ether solvent systems. After the completion of karanja oil methyl ester formation (about one and half hour later), the heating was stopped and the products were cooled and transferred to a separating funnel, where the ester layer containing mainly karanja oil methyl ester and methanol and glycerol layer containing mainly glycerol and methanol were separated. The pH of both layers was measured and neutralized separately. A known amount of sulfuric acid in methanol was added to both the layers separately to neutralize the sodium methoxide present in them. The karanja oil methyl ester was washed

for several times with distilled water to remove the methanol and other impurities. The karanja oil methyl ester, simply designated as karanja biodiesel in this paper thus obtained was dried under vacuum to remove traces of moisture. The sample of glycerol layer was also purified by similar way as in the case of methyl ester.

4. Results and Discussion

The methanolysis reaction of karanja oil was carried out with different catalytic concentrations of NaOH to optimize the catalytic concentration for this reaction to get maximum yield of karanja biodiesel and the yield of karanja biodiesel obtained in each reaction is shown in Table-1. It was found from Table-1 that the yield of karanja biodiesel is 40%, 74%, 85%, 76%, 65% and 35% at catalyst concentration of 0.5%, 0.8%, 1.0%, 1.2%, 1.4% and 1.6% NaOH of the oil, respectively. The above results revealed that the highest yield (85%) was obtained with a catalytic concentration of 1% NaOH of the oil.

The lower yield of biodiesel at lower concentration of NaOH might be due to the incomplete conversion of karanja oil. On the other hand, the lower yield at higher concentration of NaOH seems to be related to the free fatty acid of oil. Because, when the oil contains large amounts of free fatty acid, the addition of sodium hydroxide compensates this acidity and avoids catalytic deactivation, whereas for refined oil with less than 1% free fatty acid, addition of excess amount of alkaline catalyst results in the formation of emulsion, which increases the viscosity and leads to the formation of gels [12].

We then determined the fuel properties of karanja biodiesel and compared them with commercial diesel as well as with neat karanja oil (Table-2) and the comparative results are briefly discussed below.

Entry	Wt. of Methanol (g)	Wt. of Karanja Oil (g)	Conc. of Catalyst (% of Karanja oil)	Yield of Biodiesel (%)
1	11.2	100	0.5	40
2	11.2	100	0.8	74
3	11.2	100	1	85
4	11.2	100	1.2	76
5	11.2	100	1.4	65
6	11.2	100	1.6	35

Table 1: The effect of the variation of catalyst (NaOH) concentration on the yield of karanja biodiesel

Table 2: Comparative studies of fuel properties of karanja oil, karanja biodiesel and diesel

Properties	Karanja Oil	Karanja Biodiesel (Karanja Oil Methyl Ester)	Diesel
Density (gm/cc) at 15 °C	0.932	0.875	0.845
Viscosity (cSt) at 30 °C	42.54	6.53	4.06
Flash point, °C	217	158	74
Cloud point, °C	7	6	0
Pour point, °C	0	4	-2
Cetane No.	50	58.22	51
Ash content, %	0.0516	0.003	0.0005
Carbon residue, %	0.988	0.39	0.17
Sulfur content, %	0.0272	0.024	0.905
Acid value, mg KOH/g	5.49	0.423	0.34

Density: Density is an important property of liquid fuel and s correlated with particulate matter emissions. It is the weight of a unit volume of fluid. It is evident from Table-2 that the density of karanja oil, karanja biodiesel and diesel s 0.932, 0.875 and 0.845 gm/cc, respectively. A higher density for karanja biodiesel compared with commercial diesel results in the delivery of a slightly greater mass of fuel during engine operation.

Fiscosity: Viscosity is a measure of the internal friction or resistance of an oil to flow. It determines the ease of flow through pipelines, injector nozzles and orifices and the formation of fuel in the cylinder. The viscosity of karanja oil, karanja biodiesel and diesel fuel was observed to be 42.54, 6.53 and 4.06 cSt, respectively. The viscosity of karanja oil was found to be extremely high compared to its methyl ester and the diesel fuel. The Indian Standard [13] recommends the range of the viscosity of diesel from 2 to 15 cSt for use in high speed diesel engines. Thus, according to Bureau of Indian Standards, the viscosity of the karanja biodiesel meets the requirement to be used as farel.

Flash point: A key property, determining the flammability of a fuel, is the flash point. The flash point is the lowest temperature at which an applied ignition source causes the vapors of a sample to ignite. Table-2 shows that the flash point of karanja oil (217 °C) is much higher than that of diesel (74 °C). On the other hand, although the flash point of karanja biodiesel (158 °C) is higher than that of conventional diesel (74 °C), it remains within the range of American petro-diesel standard for biodiesel fuel (93–170 °C) [14].

Cloud point and pour point: Two important parameters for low temperature applications of a fuel are cloud point (CP) and pour point (PP). The CP is the temperature at which wax first becomes visible when the fuel is cooled. The PP is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow. It is evident from the Table-2 that the CP of karanja biodiesel (6 °C) is higher than diesel (0 °C) but was within the limits of cloud points suggested for vegetable oils (20 °C maximum) [15]. The PP of karanja biodiesel (4 °C) was found higher than both of karanja oil (0 °C) and diesel (-2 °C) but remained within the limit of American petro-diesel standard for biodiesel fuel (-15–10 °C) as cited in [14].

Cetane Number: Perhaps the most important characteristic of the ignition of diesel and/or biodiesel fuels is the cetane number, since it directly pertains to ignition within compression ignition engines. The cetane number is the primary specification measurement used to match fuels and engines. The cetane number of a diesel fuel is related to the ID (ignition delay) time, that is, the time that passes between injection of the fuel into the cylinder and the onset of ignition. The shorter the ID time, the higher the cetane number and vice versa. A fuel of higher cetane number gives lower delay period and provides smoother engine operation. The cetane number was calculated for karanja biodiesel as 58.22, which is slightly higher than the commercial diesel (51) and karanja oil (50) and proves the suitability of karanja biodiesel under study as a diesel fuel.

Ash Content: The percent ash content of karanja oil, karanja biodiesel and diesel was 0.0516, 0.003 and 0.0005, respectively (Table-2). The increase in ash content could be attributed to long chain of hydrocarbon and fatty acids. The ash content of karanja biodiesel was in the range as ash content specified by the Bureau of Indian Standard (0.01 maximum) [16].

Carbon Residue: The higher the carbon residue value, the greater the expected carbon deposits in the combustion chamber. Therefore, carbon residue is intended to provide some indication of relative coke forming properties. The percent carbon residue of karanja oil, karanja biodiesel and diesel was 0.988, 0.39 and 0.17, respectively (Table-2).

Sulfur Content: The concentration of SO_2 in the exhaust gas depends on the sulfur content of the fuel. Oxidation of SO_2 produces SO_3 which is the precursor of sulfuric acid, responsible for the sulfate particulate matter emissions. Sulfur oxides have a profound impact on environment being the major cause of acid rains. Present investigation (Table-2) reveals that the sulfur content of karanja biodiesel (0.024%) is much less than that of diesel (0.905%).

Acid Value: Petroleum products may contain acidic constituents present as additives or as degradation products, such as oxidation products during service. The acid value can be used as a guide in quality control of fuels. The acid value of karanja oil, karanja biodiesel and diesel was observed as 5.49, 0.423 and 0.34 mg of KOH/gm, respectively. It was found from Table-2 that the acid value of karanja biodiesel was in the range recommended for diesel fuel by Indian Standard (maximum 0.50 mg of KOH/gm) [16].

5. Conclusion

We have demonstrated the production of biodiesel from karanja oil through transesterification with methanol in presence of sodium hydroxide catalyst. Incomplete transesterification and separation may produce karanja biodiesel of low quality. Thus, the reaction should be completed and the glycerol and karanja biodiesel layers should be separated completely. The fuel properties such as viscosity, ash content, carbon residue, flash point and acid value of neat karanja oil was found to be higher than that of diesel which make it unsuitable for use as fuel in diesel engines. On the other hand, the esterification of karanja oil to its biodiesel made the fuel properties closer to that of diesel. Moreover, it has the following advantages over diesel fuel: as a neat fuel it produce less smoke and particulates, has higher cetane number and low sulfur content, it is biodegradable and non-toxic. Thus, the study has enabled us to confirm that karanja oil can be used as a raw material to obtain biodiesel, which can be used as fuel in diesel engine in order to reduce the environmental impact of fossil fuels.

References

- Kloptenstem, W. E., 1988, "Effect of molecular weights of fatty acid esters on cetane numbers as diesel fuels", J. Am. Oil Chem. Soc., 65, pp 1029–1031.
- Harrington, K. J., 1986, "Chemical and physical properties of vegetable oil esters and their effect on diesel fuel performance", Biomass, 9(1), pp 1–17.
- Masjuki, H. S., 1993, "Biofuel as diesel fuel alternative: an overview", J. Energy Heat Mass Transfer, 15, pp 293–304.
- LePori, W. A., C. R. Engler, L. A. Johnson and C. M. Yarbrough, 1992, "Animal fats as alternative diesel fuels, in liquid fuels from renewable resources", Proceedings of an Alternative Energy Conference. American Society of Agricultural Engineers, St Joseph, pp 89–98.
- Rao, S. P. and V. K. Gopalakrishnan, 1991, "Vegetable oils and their methyl esters as fuels for diesel engines", Ind. J. Technol., 29, pp 292–297.
- Masjuki, H. and M. Sohif, 1991, "Performance evaluation of palm oil diesel blends on small engine", J. Energy Heat Mass Transfer, 13, pp 125–133.
- Nag, A. and K. B. de Bhattcharya, 1995, "New utilizations of vegetable oils", J. Am. Oil Chem. Soc., 72(12), pp 1391– 1393.
- Takeda, Y., 1982, "Developmental study on jatropha curcas (Sabu dum) oil as a substitute for diesel engine oil in Thailand", J. Agricultural Assoc. China, 20(1), pp 1–9.
- Piyaporn, K. J. Narumon and K. Kanit, 1996, "Survey of seed oils for use as diesel fuels", J. Am. Oil Chem. Soc., 71(4), pp 471–477.
- 10. Vivek and A. K. Gupta, 2004, "Journal of Scientific and Industrial Research", 63(1), pp 39-47.

- **11** Demirbas, A., 2003, "Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey", Energy Convers. Manage., 44, pp 2093–2109.
- Enciner, J. M., J. F. Gonzalez, J. J. Rodriguez and A. Tajedor, 2002, "Biodiesel fuel from vegetable oils: Transesterification of *Cynara cardunculus* L. oil with ethanol", Energy Fuels, 16, pp 443-450.
- Bureau of Indian Standards, New Delhi, 1976, "Diesel Fuel Specifications", IS: 1448, pp 25.
- Rashid, U., F. Anwar, A. Jamil and H. N. Bhatti, 2010, "Jatropha curcas Seed Oil as a Viable Sourse for Biodiesel", Pak. J. Bot., 42(1), pp 575-582.
- Hawkins, C. S. and V. Fuls, 1982, "Comparative Combustion Studies on Various Plant Oil Esters and the Long Term Effects of an Ethyl Ester on a Compression-Ignition Engine", Proc. International Conference on Plant Oils as Fuels, American Society of Agricultural Engineers, St. Joseph, pp 374-383.
- 16. Bureau of Indian Standards, New Delhi, 1974, "Diesel Fuel Specifications", IS: 1448, pp 10.