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Production of Rubber Seed Oil Based Biodiesel Using Different Catalysts

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ABSTRACT

Biodiesel was obtained from crude and refined rubber (*Hevea brasiliensis*) seed oil (RSO) by transesterification using different catalysts: sodium hydroxide (1), sodium metal (2), sulphuric acid (3), phosphoric acid (4), clay acid (5) and alkaline (6) activated. The yield, physico-chemical and fuel properties of the biodiesel were determined. The physico-chemical and fuel properties were compared to that of the commercial diesel fuel. The methyl ester yield from the crude RSO were in the order of III>IV>II>V>VI>I and that of the refined oil were of the order: II>I>III>IV>VI>V. On a general note, sample I formulated from the crude RSO which is sodium hydroxide catalyzed gave the least yield of 15% while sample II formulated from the refined RSO which is sodium metal catalyzed gave the highest yield of 92.1%. Comparative analyses of the properties of the biodiesel to that of commercial diesel fuel showed that transesterification improved the fuel properties of the oil. The viscosity, %free fatty acid values were reduced, while the calculated fuel potential increased. Other fuel properties were found to be in accordance with the ASTM standards.

Key words: Rubber seed oil, biodiesel, transesterification, yield, catalyst and fuel properties

INTRODUCTION

The depletion in crude oil reserves arising from the extensive consumption of fossil fuel has caused an increased awareness of environmental issues resulting from such depletion. The craving for an alternative renewable and eco-friendly source of energy arises. One of such is biodiesel.

Biodiesel is a fatty acid alkyl ester, normally produced by transeterification process. Transeterification also is the replacement of an alcohol from an ester by another alcohol usually of low molecular weight (Assman *et al*., 1996; Stildham *et al*., 2000; Wimmer, 1995). It is a reversible reaction and the rate of conversion to the fatty acid alkyl ester is greatly affected by several factors such as type of catalyst, molar ratio of alcohol to oil, stirring, etc. (Morrison and Boyd, 2004). Catalysts used in transesterification include alkalis, acids, enzymes and also heterogeneous catalyst. However, alkali catalysts (sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide) are more effective (Fangrui and Hanna, 1999). For oils with high free fatty acid content and moisture, acid catalyzed transesterification is more suitable. Therefore, the choice of catalyst for transesterification reaction is largely dependent on the nature of oil, such as, level of purity, level of percent free fatty acid (%ffa) etc. Transesterification reaction involving alkaline catalyst is known to give higher yield especially for pure oil (with low %free fatty acid) where low yield is likely to be the result with impure oils (with high %free fatty acid) (Dorado *et al.*, 2002). Also, the difficulties observed in separation, both in refining and transesterification, of the soap stocks/oil and soap stock/ methyl ester, in the respective processes warrants the need for a more convenient and less laborious method of biodiesel production, while considering the yield of the product (Dorado *et al.*, 2002).

In this study, samples of crude and refined rubber seed oil were employed in the preparation of methyl esters using different types of catalysts, such as, alkaline (NaOH/Methanol and Na/Methanol), acid (H_2SO_4 and H_3PO_4) and activated clay (alkali and acid activated), so as to determine their yield and consequently, ascertain which type of catalyst is more suitable for specific type of oil.

MATERIALS AND METHODS

Sample collection and preparation: Rubber seeds were collected from the plantation of Rubber Research Institute of Nigeria, Iyanomo-Benin City, Nigeria. They were dried, cracked, milled and the oil extracted with soxhlet. Part of the oil was subjected to refining.

Clay preparation: The clay sample was prepared according to Li *et al.* (2007) method.

Clay activation

Acid and alkaline activation of clay: One hundred and fifty grams of prepared clay was mixed with 200 mL of 2 M H_2SO_4 solution for acid activation and 2 M NaOH solution for alkaline in a 1000 mL beaker. The mixture was stirred and diluted with distilled water up to 800 mL mark of the beaker and was allowed to settle for 24 h. The water phase was gently decanted. The acid treated or alkaline modified clay was placed in a crucible and oven dried for 3 h at a temperature of 180-200°C. The dried activated clay was pulverized and sieved using 100 μm mesh size.

Refining of rubber seed oil

Degumming: Three hundred grams of crude RSO was weighed, mixed with 20 mL of phosphoric acid in a 500 mL beaker, stirred and allowed to settle in a separating funnel over-night and finally the gums was separated from the RSO.

Neutralization of the degummed Rubber Seed Oil (RSO): Two hundred grams of degummed RSO was weighed into a 500 m beaker and then subjected to heat maintained at the temperature of 60°C and was subjected to stirring, 150 mL of 0.8 M NaOH solution was gradually added. Stirring was allowed for 5 min and the solution was allowed to settle for about 15 min followed by separation. After separating the soap stock from the degummed RSO, the oil was washed with hot water until the remaining of oil was free from soap stock. After the neutralization process, the neutralized RSO was dried and then analyzed for % FFA.

Transesterification methods

Transesterification using acid as catalyst: Into a two 500 mL quick fit conical flask, methanol (84 mL), concentrated sulphuric acid/ phosphoric acid (6 mL) were charged, then the crude rubber seed oil and refined RSO (90 mL) were added gradually while stirring reflux for three hours at about 105°C. The reaction mixtures formed were allowed to cool, were extracted with n-heptane to obtain a heptane/methyl ester mixture and the glycerol lower layer was run off. The mixture was neutralized with sodium hydrogen bicarbonate, washed with distilled water and dried over unhydrous sodium sulphate and later disolventised to obtain a clear golden yellow, less viscous, rubber seed oil methyl ester (Mittelbach *et al.*, 1995).

Transesterification using base as catalyst: The alkoxides used in the reaction were prepared by dissolving 0.1 wt% sodium hydroxide in methanol and sodium metal in methanol in a 0.1 g:10 mL ratio respectively in a conical flask and left overnight. Tow hundred milli litter of RSO was gradually added to the alkoxides in the conical flask, under a reflux condenser and a stirring device, while heating at 60°C for 15 min. The two layer mixture formed thereof was extracted with n-heptane to obtain the methyl ester and glycerol layer run off. The methyl ester/n-heptane mixture left was washed with warm distilled water until neutral pH, after which the solvent was removed to obtain a clear, golden-yellow, less viscous methyl ester (Feuge and Grose, 1949).

Transesterification using clay as catalyst: One hundred gram of methanol and 10 g of the activated clays (acid and alkaline activated) were mixed under refluxed at 80°C for 1 h as the catalyst activation step. The ratio of methanol: RSO is kept constant at 2:5 without any changes. Secondly, the 250 g of RSO had been added to transesterify for 6 h, the weight ratio among methanol: catalyst: RSO was 10:1:12. The solution was filtered to remove catalyst particles and impurities prior to biodiesel analysis. The glycerol/methyl ester layer was separated (Wan *et al.*, 2009).

Characterization of samples: The physico-chemical properties of the Rubber Seed Oil (RSO) and the methyl esters were determined using ASTM standard methods (ASTM D 1639-90, 1994; ASTM D 1541-60, 1979; ASTM D 1962-67, 1979).

Biodiesel properties of the RSO and its methyl esters were determined using ASTM standard methods (Nadkarni, 2007).

RESULTS AND DISCUSSION

The physical and chemical properties of the crude and refined oils are shown in Table 1. The colours of the crude and refined oils were both golden yellow respectively because the crude RSO was chemically extracted. The results show that refining of the oil decreases the acid value, % free fatty acid (%FFA) and viscosity. This could be explained by the fact that refining removes impurities and contaminants present in the oil which include pigments, non hydratable lecithin, oxidized fats and many other non-lipid materials (Hoffmann, 1986; Kai *et al.*, 2010). The reaction

Table 1: Physico-chemical properties of Crude RSO and Refined RSO

Property	Crude RSO	Refined RSO
Colour	Golden yellow	Golden yellow
Specific gravity (ambient temp.)	0.9209	0.912
Acid value (mg KOH g^{-1})	42.412	1.3
FFA (%)	23.471	0.6
Iodine value (g I_2 /100 g)	140.06	142.60
Saponification value (mg KOH g^{-1})	191.37	191.50
Viscosity (cSt) at 40°C	38.10	26.97
Fuel potential, KJ Kg^{-1}	39,727.2	39,915.7
Cetane number	49.73	49.83

cSt means centistroke

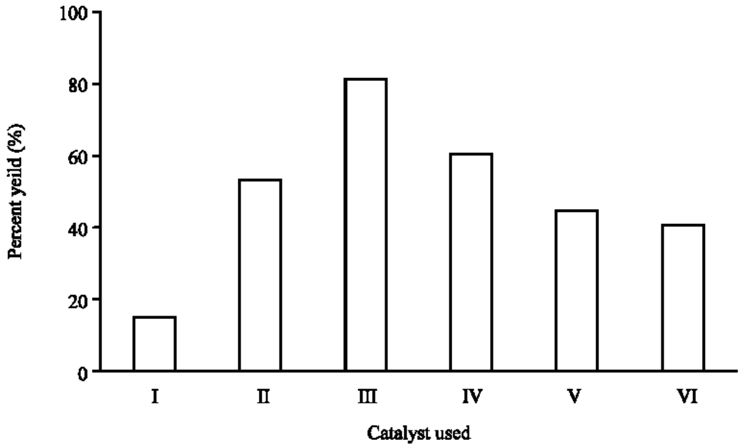

Fig. 1: Ester yield of the crude RSO

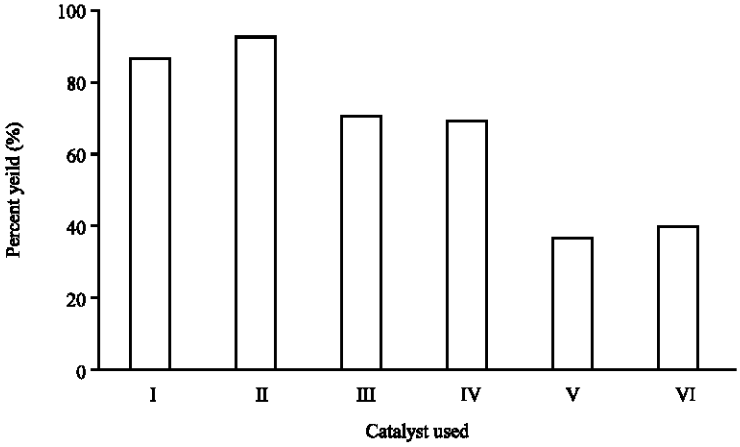

Fig. 2: Ester yield of the Refined RSO

showed an iodine value of 140.06 for crude RSO and 142.60 for the refined RSO. Acid values of 42.41 mg KOH g^{-1} for crude RSO and 1.30 mg KOH g^{-1} for the refined RSO, respectively. The % FFA, viscosity, fuel potential, cetane number, saponification values are as follows: 23.471, 38.10, 39727.7, 49.73 and 191.37, respectively for the crude RSO, while 0.6, 26.97, 39915.7, 49.83 and 191.50, respectively for refined RSO. To complete alkali catalyzed reaction, a Free Fatty Acid (FFA) value lower than 3% is needed (Dorado *et al.*, 2002).

The specific gravity of both the crude RSO and refined RSO investigated were 0.92 and 0.91 which implies that it is less dense than water. These properties of rubber seed oil showed that it can be successfully utilized for biodiesel production.

Methyl ester yield: The yield of methyl esters of crude and refined RSO are shown in Fig. 1 and 2. In Fig. 1, the highest yield in the transesterification reaction was obtained when sulphuric acid catalyst (III) was used and gave a yield of 81.5% conversion, followed by a conversion of 60% when catalyst phosphoric acid (IV) was used in the transesterification process. The use of sodium metal catalyst in the transesterification of crude RSO gave yield that would encourage the used of it as

Table 2: Fuel properties of crude RSO methyl esters

Property	I (NaOH)	II (Na-Metal)	III (H_2SO_4)	IV (H_3PO_4)	V (Clay-acid activated)	VI (Clay-alkali activated)	Biodiesel (ASTM)
Specific gravity (ambient temp.)	0.884	0.863	0.876	0.892	0.860	0.869	0.8900
Acid value (mg KOH g^{-1})	0.300	0.260	0.670	0.380	0.230	04.000	0.5000
Viscosity (cSt) 30°C	6.220	6.830	6.690	6.270	6.290	6.480	1.9-6.0
Fuel Potential MJ Kg^{-1}	40.340	40.370	40.540	40.350	40.200	40.550	-
Cloud Point (°C)	0.300	0.300	0.400	0.300	0.300	0.400	-
Flash Point (°C)	239.000	233.000	235.000	236.000	230.000	235.000	130.000
Fire Point (°C)	269.000	276.000	273.000	270.000	286.000	274.000	-
Cetane No.	49.970	49.950	50.010	50.000	49.950	50.080	≥47.000
% Yield	15.000	53.000	81.500	60.000	45.000	40.500	-

cSt Means centistroke

Table 3: Fuel properties of refined RSO methyl esters

Property	I (NaOH)	II (Na-Metal)	III (H_2SO_4)	IV (H_3PO_4)	V (Clay-acid activated)	VI (Clay-alkali activated)	Biodiesel (ASTM)
Specific gravity (ambient temp.)	0.886	0.872	0.883	0.879	0.876	0.885	0.8900
Acid value (mg KOH g^{-1})	0.170	0.300	0.230	0.410	0.310	0.270	0.5000
Viscosity (cSt) at 30°C	6.250	6.320	6.880	6.760	6.680	6.020	1.9-6.0
Fuel potential MJ Kg^{-1}	40.320	40.350	40.470	40.340	40.570	40.470	-
Cloud point (°C)	0.700	0.400	0.400	0.300	0.600	0.700	-
Flash point (°C)	236.000	240.000	244.000	232.000	239.000	241.000	130.0000
Fire point (°C)	280.000	273.000	297.000	266.000	282.000	278.000	-
Cetane No.	49.900	49.930	50.050	49.980	50.090	50.040	≥47.0000
% Yield	86.700	92.100	70.600	68.700	36.800	40.300	-

catalyst, with a conversion yield of 53%. The activated clays (V and VI) also were able to give yield better than NaOH catalyzed transesterification, though the percent yield were below average, which could be as a result of the loss of the methyl ester during separation and washing.

The percent yield of the methyl esters are in the order III>IV>II>V>VI>I. The low yield of sodium hydroxide catalyzed transesterification is in agreement with an earlier studies (Carr, 1976; Turck, 2002) which is as a result of the esterification of the FFA by some of the catalysts to form soap and other by-products. During the washing process there is loss of methyl ester which forms emulsion with soap, so there is difficulty in separation.

In Fig. 2, the percent conversion of the refined RSO to esters gave yield better than the crude RSO. This higher ester fuel yield could be attributed to the reduction in impurities and acid value which would have interfered with the reaction process. These suggest that for base catalyzed transesterification, insufficient alkali would have been available for catalysis (Markley, 1960). The relative order of effectiveness is II>I>III>IV>VI>V.

Biodiesel properties: The important biodiesel properties of rubber seed oil as measured are presented in Table 2 and 3. These properties of rubber seed oil methyl esters investigated in this study are compared with standard specification for biodiesel (ASTM D 6751) (Kannan and Marappan, 2011).

The specific gravity of the biodiesels obtained from crude RSO and refined RSO in the present study as shown in Table 2, 3, are 0.884, 0.863, 0.876, 0.892, 0.860 and 0.869, respectively and

0.886, 0872, 0.883,0879, 0.876 and 0.885, respectively. The specific gravity obtained for the RSO biodiesel falls within the limit specified by ASTM for biodiesel in Table 3. From the results of this study, the specific gravity of RSO biodiesel is in very good agreement with the above biodiesel standards (Baroutian *et al.*, 2008).

Biodiesel has higher viscosity than conventional diesel fuel which is in agreement with reports from several researchers (Graboski and McCormick, 1998; Knothe and Steidley, 2005; Peterson, *et al.*, 1990; Yuan *et al.*, 2004). The RSO biodiesel viscosity obtained in Table 2 and 3 is almost three times the viscosity of the fossil diesel as found in alcohol esters of rapeseed, canola, soybean and beef tallow (Van Gerpen, 2005). The value also falls within the specified limits by ASTM D6751 standards. The reported technical implication of higher viscosity of biodiesel is that it decreases the leakages of fuel in a plunger pair and in turn it changes the parameters of a fuel supply process (Lebedevas and Vaicekauskas, 2006).

Other fuel properties such as fire point, cloud point, flash point and fuel potential obtained in Table 2 and 3 for RSO biodiesel compared to conventional petroleum based diesel as well as lower gross and net heat of combustion obtained for fossil diesel was found to be consistent with earlier findings on such biodiesel fuel like alcohol esters of rapeseed, canola, beef tallow, soybean and Midwest biofuel methyl soyate (Abigor *et al.*, 2000; Graboski and McCormick, 1998; Schwab *et al.*, 1987). According to ASTM standard D 6751, no limit is specified for cloud point. The reason is that the climate conditions in the world vary considerably, thus affecting the needs of biodiesel users in a specific region (Rashid and Anwar, 2008).

CONCLUSION

The results obtained from the study show that the refined rubber seed oil gave the highest yield of biodiesel compared to that of the crude rubber seed oil. Sodium metal catalyst gave the highest yield for the refined oil and sulphuric acid catalyst gave the highest yield for the crude oil. A very low yield was obtained from sodium hydroxide and acid activated clay catalyzed reaction for the crude and refined oil, respectively.

Sodium metal and sodium hydroxide catalyst will be more suitable for transesterification of refined rubber seed oil, while sulphuric acid and phosphoric acid catalyst would be suitable for crude rubber seed oil. The use of heterogeneous catalyst (clay) should be encouraged, because it saves cost.

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