Physicochemical Properties of Rubber (*Hevea brasiliensis*) Seed Oil, Its Biodiesel and Blends with Diesel

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Authors' contributions

The work was carried out by both authors. Both authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Literature search shows that research on feed stocks for the production of biodiesel in Africa have not been well documented. To close this gap, a research project was initiated to measure the fuel and physicochemical properties of common vegetable oils in Nigeria. The works on cashew nut oil has been reported and that of rubber seed oil is being reported in this paper. Rubber tree seed oil has several industrial applications but not all the fuel and physicochemical properties are available in literature, hence the aim of this study is to provide the properties of not only the oil but also the biodiesel, 20% and 10% blends with diesel. For the purpose of characterization, the oil was extracted by soxhlet extraction and the free fatty acids was measured and found to be 23.68 % which can react with the sodium hydroxide catalyst to form soaps that can inhibit the separation of the esters and glycerin. To prevent this, acid catalyst was first used to neutralize and reduce the high level of free fatty acids in the oil to less than 2% before using sodium hydroxide for the transesterification process. The resulting biodiesel was washed, dried and blended 20% and 10% with diesel. The fatty acid profiles were determined by chromatography analyzer and the oil was found to be unsaturated. The characterization of the oil, its biodiesel, and the blends were done according to ASTM and EU methods and the results obtained show that the properties of the biodiesel and blends are similar to those of diesel which shows conclusively that it can be used as alternative fuel for diesel engines.

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ABBREVIATIONS

ASTM: American Society for Test and Materials, AOSC: American Oil chemist Society, EN: European Norms.

1. INTRODUCTION

Rubber tree (*Hevea brasiliensis*) is the source of latex that is a feed stock for the production of rubber tyres used on motor vehicles, motor cycles and bicycles. It also produces seeds which are usually allowed to drop to the ground to decay despite having a yield of seeds per annum estimated at 100-150 kg/ha [1] and seed oil content of 35 - 40% [2]. It is inedible and so does not compete with food, but is eaten by cows in Nigeria notwithstanding the fact that it contains cyanogenic glycosides which will release prussic acid in acidic condition. The oil is unsaturated and semidrying and can hence be used in the manufacture of paint, soap, alkyd resin and wood polish. The potential for using it as a feed stock for biodiesel (methyl ester) production has been investigated severally by [3,4] and [5]. The characterization of rubber seed oil and its biodiesel have also been undertaken by [3] but limited to the oil and biodiesel. This present study is a more comprehensive characterization of the physicochemical and fuel properties of rubber seed oil (RSO), its biodiesel (B100), (10%) B10 and (20%) B20 blends with diesel, which is the ratio that gives the nearest property to diesel. Biodiesel is the mono alkyl esters obtained by the transesterification of vegetable oil and animals fats [6]. Their fuel properties are better than those of diesel as regards biodegradability, environmental friendliness, nontoxicity, replenishable agricultural source, reduced harmful exhaust emissions and lower fire risk than diesel [7,8,9,10,11]. The fuel properties of biodiesels vary with the type of vegetable oil used, where they were grown, the method of oil extraction and refining [12]. Biodiesel fuel standards are derived from those used for diesel, to allow for consistent standard of biodiesel even when different vegetable oils are used and set limits for impurities such as triglycerides, monoglycerides, diglycerides, water content, soap and residual alcohol. These impurities must not be excessive as they can lead to their deterioration during storage as well as to significant operational problems. The aim of this study is primarily to provide data on the characterization of not only rubber seed oil, its biodiesel, but also B10 and B20 blends with diesel which has not been comprehensively done before except for cashew nut oil by [13].

2. MATERIALS AND METHODS

2.1 Oil Extraction

2 kg of rubber seeds of indigenous clone was obtained from rubber research institute of Nigeria's farm in Edo state of Nigeria. They were dried in the sun at 35ºC, which reduces moisture content to 7% [14], after which they were decorticated manually to separate the kernels from the shells. The kernels were milled to reduce their diameters and to allow for faster and more oil extraction [15,16]. The oil was extracted in a soxhlet extractor with *n*-hexane as the solvent and operated at 60ºC. The residual *n*-hexane in the oil was removed in a vacuum rotary evaporator operated at 75ºC. The oil obtained was weighed and the percentage oil yield was calculated using equation (1).

$$\text{Oil yield } \% = \frac{\text{weight of oil extracted}}{\text{weight of seed kernels used}} \times 100 \quad (1)$$

2.2 Characterization of the Oil

The Free Fatty Acid (FFA) value of the oil (oleic acid %) was first measured by titrating with alcohol, phenolphthalein and sodium hydroxide until the pink colour appeared, to determine if pretreatment was necessary or not before alkaline transesterification. The FFA value for the oil was 23.68% which was too high for direct alkaline transesterification [17] as values higher than 2% can lead to unnecessary soap formation that can inhibit biodiesel yield.

2.3 Transesterification Procedure

Transesterification was carried out using a laboratory scale biodiesel processor. The oil was first esterified with anhydrous methanol at a molar ratio of 9:1 using 1% (v/v) sulfuric acid (H_2SO_4) as catalyst to transform the FFAs to ester and reduce the value to less than 2% [3,18,19].

Methanol, which is low cost, short-chain and fast reacting was used as the reagent [20]. Sulfuric acid is also low priced and has high catalytic activity. Additionally, it is hygroscopic, which is essential in absorbing the water released from the reaction mixtures [20]. The pretreatment also aided the removal of phosphatides (Acid degumming) which helps fuel quality because phosphatides promote the accumulation of water in the ester product [21]. The alkaline transesterification was done using methanol at a volume ratio of 4 to 1 and sodium hydroxide as catalyst at 3 g/litre. The reactor was stirred continuously for 5 hours at 600 rev/min. and a constant temperature of 60ºC at the end of which it was poured into a glass bottle and stored overnight for the reaction to reach equilibrium and separate into biodiesel and glycerol. The glycerol and biodiesel were separated and the biodiesel was washed as described in [13]. Finally, the washed biodiesel was dried by passing it through anhydrous sodium sulphate (Na_2SO_4) [22] because drying ordinarily by applying heat would polymerize the biodiesel and render it useless.

2.4 Fatty Acid Profile

The fatty acid profile of the rubber seed oil (RSO), the B100, B10 and B20 and the standard sample of free fatty acid were determined as reported by [13,23] using the HP 6890 Gas Chromatography analyzer powered by HP ChemStation Rev A 09.11 [1206] software and equipped with a flame Ionization Detector (FID) and following the modified AOAC 965.49 and AOAC 996.06 official methods and using nitrogen as the carrier gas and an initial oven temperature of 60ºC.

2.5 Determination of Fuel and Physico-chemical Properties

The fuel and physicochemical properties of the rubber seed oil, it's biodiesel and the blends were determined following ASTM, EN and AOCS methods and the results obtained are similar to those by [3]. The equipment used and the procedures are similar to those reported for cashew nut oil [13] and are as follows.

2.5.1 Density and relative density

To measure the density and relative density, the hydrometer was used to IP-160/ASTM D-1298 protocol. The measurements were made in triplicate and then averaged.

2.5.2 Pour and cloud points

A 50 ml sample initially at 45ºC was cooled in Herzog HCP852 at specified rate. Checks were made at intervals of 3ºC until the sample stopped flowing. A cloud point meter equipped with a waveguide sensor of a total-reflection type as reported by [23] was used to determine the cloud point.

2.5.3 Cold Filter Plugging Point (CFPP)

A Herzog CFPP analyzer, model MC 840 was used to estimate the cold filter plugging point which is the lowest temperature at which a fuel will give trouble free flow in certain fuel systems according to EN 116. It is an important test for fuel to be used in cold region when biodiesel can freeze and starve the engine of fuel.

2.5.4 Dynamic and kinematic viscosities

The dynamic viscosity was determined using Brookfield equipment model LV-DVII, coupled to a heat controller at a temperature of 30ºC using a small sample adaptor while the kinematic viscosity was measured with capillary viscometer in which the time for a given volume of the fuel sample to flow through the capillary under gravity was measured. The equipment used was Herzog GmbH MP – 480 and the viscosity was calculated using equation (2).

$$Kinematic\ viscosity =$$

$$\frac{calibration\ constant\ \left(\frac{mm^2}{s^2}\right)}{Mean\ time\ of\ flow\ (s)}\ (2)$$

2.5.5 Flash point

2.2.5. The flash point was determined according to ASTM D6751 using the Kehler Model K-16270 flash point apparatus.

2.5.6. Heating values

The lower heating value was determined by burning the fuel in an oxygen bomb calorimeter (Parr Instrument Company, US) according to ASTM D240 protocol.

2.5.7 Cetane index

The cetane indices of samples were computed using equation 2 [24].

$$CI = -420.34 + 0.016G^2 + 0.192G(logT_{50}) + 65.01(logT_{50})^2 - 0.0001809T_{50}^2 \quad (2)$$

Where G is the specific gravity as specified by the American Petroleum Institute, while T_{50} is the distillation temperature at 50 vol.% fuel sample distilled and condensed in a unit of °F. The results were cross checked using a cetane index meter.

2.5.8 Iodine, peroxide and saponification values

The iodine, peroxide and saponification values were analyzed, by titration according to [25] and calculating the values by equations (3), (4) and (5).

$$Iodine\ value = \frac{(B-T)xCx0.001269}{Y} \quad (3)$$

$$Peroxide\ value = \frac{(T-B)xCx1000}{Y} \quad (4)$$

$$Saponification\ value = \frac{(B-T)x28.5}{Y} \quad (5)$$

where B and T are denoted as the amounts (in ml) of sodium thiosulfate titrated for the blank sample and tested sample, respectively; C is the molar concentration (in mol/l) of sodium thiosulfate; and Y is the weight (in g) of the tested sample.

2.5.9 Acidic number

The acid value (mgKOH/g) was determined according to ASTM D664 using equation (6)

$$Acid\ Number = \frac{56.1VxC}{Y} \quad (6)$$

Where V = Volume of sodium hydroxide used for titration (ml), C = Concentration of sodium hydroxide used for titration (mol/l) and Y = mass of sample used for analysis (g).

2.5.10 Oxidative stability

The oxidative stability test was conducted in a glass ware apparatus to ASTM D 2274. The accelerated degrading of the samples was done by applying heat and bubbling with oxygen for 16 hours at a constant temperature of 95ºC. After this duration, the insolubles formed were collected by filtration and then measured. The duration that the fuel can be stored before

deterioration by acidification was estimated as reported in (13).

2.5.11 Soap content

For soap content measurement, the AOCS method cc 17-79, (soap in oil) was used. 5 g of each sample were titrated with 0.1N solution of HCL acid to the phenolphthalein end point. 1 ml of bromophenol blue indicator was added and the titration was continued until the bromophenol changed from blue to yellow.

2.5.12 Cold soak filtration

To determine the cold soak filtration, 350 ml of the samples were chilled for 16 hours at 4ºC in Neslab RTE-740 digital plus refrigerated bath from Thermo Scientific (NH USA). After chilling, the samples were removed and the times of removal for each sample were recorded. The samples were allowed to cool to 20ºC without external heating. The samples were next filtered under vacuum between 533 - 635 mmHg through an 0.7 micron glass fiber filter with stainless steel support within 1 hour after reaching 20ºC.

2.5.13 pH value

The pH values of the neat oil, biodiesel and blends were determined by a pH meter.

2.5.14 Moisture content

The Karl-Fisher Method (ASTM D 6304) 831 KF Coulometer (Metrohm Company, Switzerland) was used to measure the moisture content of 5 ml of each of the samples.

2.5.15 Carbon residue

Carbon residue test was conducted by heating the fuel at a controlled rate to 500ºC in a chamber filled with nitrogen to make the sample coke without burning. The mass of the remaining coke measured after flushing out the volatile compound with nitrogen. The intention here is to simulate how carbon deposits are formed in the engine.

2.5.16 Sulfated ash

The residue was treated with sulfuric acid and heated in an Isotemp muffle furnace to 750ºC for the carbon to be completely oxidized before allowing it to cool down to room temperature.

The resulting ash formed was again treated with sulfuric acid and heated to 750ºC until the weight became constant. The percentage ash content was calculated by dividing the final weight by the initial weight and multiplying by 100.

2.5.17 Water and sediment

100 ml of the fuel sample was spun at 800 rev/min for 10 minutes in a centrifuge model HNS II (Thermo Electron Corp, US). The amount of water and sediment that settled in the tip of the centrifuge was then read to 0.005 ml as the percentage water and sediment.

2.5.18 Alkaline metals analysis

The Teledyne Fuelpro biodiesel metal analyzer was used to determine the alkaline metals, phosphorous and sulphur contents. 50 ml of each biodiesel sample was first mixed with kerosene in the ratio 1:10. The purpose of the dilution was to eliminate any viscosity effects that can lead to error. The analyzer was calibrated using standards formulated by diluting pure biodiesel stock standards. The concentration of the standards was 0.00, 10.00, 20.00, and 30.00. 40.00 ppm of Na, K, Ca, mg, P and S.

2.5.19 Glycerine content

The wet AOCS Official method Ca 14-56 was used for the determination of the glycerine content. It is similar to the method prescribed in the ASTM standard but easier to perform. It was also used for the determination of monoglycerides, diglycerides and triglycerides (13).

2.5.20 Vacuum distillation

The vacuum distillation temperature was determined using the ASTM D1160 reduced pressure Advanced Distillation Curve (DAC) apparatus. The system pressure was set between 1 kpa and 83 kPa. The uncertainty was less than 1ºC for all measurements. Distillation temperatures were selected to correspond to 5 to 95 volume % at interval of 5 volume % of the liquid fuel distilled and condensed. The distillation results were used to calculate the cetane index according to EN ISO 4264 standard.

2.5.21 Copper strip corrosion test

This test was undertaken according to ASTM D130 procedure. A piece of copper strip was polished and dipped into 50 ml of the oil at a constant temperature of 60ºC. After 3 hours, the strip was removed and washed in a solvent, and the tarnish and corrosion were compared with those of standard scale for quantification. The procedure was repeated for the B100, B10, and B20. This test is important because many parts of the fuel system and fuel tank are made from copper or copper alloys and are liable to corrosion when exposed to the fuels.

3. RESULTS AND DISCUSSION

Rubber seed oil at room temperature was black in colour but turned dark brown after transesterification and blending. It was very sensitive to heat and turned to latex when heated beyond 110ºC. The implication is that B100 cannot be effectively dried by heating. The oil content was 40.4%. All the discussion refers to the results shown in Tables 1, 2 and 3.

3.1 Fatty Acid Profile

The fatty acid profiles of RSO, B100 and B20 are shown in Fig. 1. The oil contains 19% of palmitic and 3.876 % of stearic acids both of which are saturated, and 23.7% of oleic, 37.7% of linoleic and 15% of linolenic acids. Making it 76.8% unsaturated. The profile for biodiesel followed the same pattern, but the volume of the acid with double and triple bonds decreased while that of the monounsaturated increased making the total unsaturation to reduce from 76 to 74%. Of particular significance is the oleic acid of 27% for the B100 which is close to the value obtained by [3] but well below the average value of 45% for vegetable oils [23]. Oleic acid value determines the balance between cold flow properties and oxidation stability and tendency for soap formation during transesterification. Many properties vary with chain length, number of bonds and degree of unsaturation [26]. It was reported that biodiesel of saturated oils have higher cloud point, cetane number and better stability [3]. The effect of blending on the fatty acids is very marginal as earlier reported by [27].

3.2 Density

The oil had a density of 910 kg/m^3 which reduced to 877 kg/m^3 for B100, 855 kg/m^3 for B20 and 857.7 kg/m^3 for B10. Density is important as it affects several engine performance variables including fuel mass flow rate, fuel pump performance, spray pattern and depth of

penetration. It has been reported that an increase in density from 860 to 885 kg/m^3 for biodiesel will increase the viscosity from 2.59 to 4.63 mm^2/s and the increases are highly regular [28,29]. The changes in relative density follow the same pattern and both properties are with the ASTM limits for biodiesel.

3.3 Cloud, Pour and Cold Filter Plugging Points

These tests are very important for biodiesel because if the fuel freezes at low temperature, the fuel filter will be partially plugged and fuel flow would be restricted, which can stall the engine.

Table 1. Properties of rubber seed oil, its Ester and Blends according to ASTM D6751-02 and EN 14214

Property	Rubber seed oil	B100	B10	B20	ASTM D6751-02	EN 14214
Density kg/m^3 at 25ºC	910	877.3	855	857.7		860-900
Relative density kg/m^3 at 15ºC	0.911	0.878	0.856	0.858		
Cloud point ºC	25	9	8	1		
Pour point ºC	18	7	5	9		
Cold filter Plug Point ºC	22	8	6	10		
Flash point ºC	165	141	83	91		120 min
Dynamic viscosity (mN s/m^2) at 40ºC	67.72	5.07	2.53	2.84		
Kinematic viscosity (mm^2/s)at 40ºC	74.31	5.77	2.96	3.31	1.9-6.0	3.5-5.0
Lower heating value (KJ/kg)	40	37.15	42.8	42.15		
Higher heating value (KJ/kg)	37	40.3	45.35	44.8		
Cetane number	46.3	52.56	45.39	46.03	47 min	51 min
Free fatty acid %	23.68	0.225	0.301	0.263		
Acid value (mgKOH/g)	47.12	0.448	0.599	0.523	0.80 max	0.05 max
Iodine value (gI$_2$/100g)	106	101.01	17.77	29.90		120 max
Peroxide value (gI$_2$/100g)	25.30	29.00	16.30	17.70		
Oxidation stability (hours) 110ºC	17	8	0.8	1.5		6 min
pH value	7.4	7.90	8.63	8.43		
Saponification value (mgKOH/g)	183.7	193.5	162.2	166.9		
Soap content %	0	8	0.8	1.5		
Cold soak filtration ºC	320	215	81	98		
Water and sediments % vol	13.00	0.04	0.005	0.008		500 max
Moisture content (ppm)	3530.0	264	29	57		
Refractive index at 15ºC	1.467	1.343	1.480	1.408		
Sulfated ash % (mol/mol)	0.90	0.03	0.01	0.01	0.02 max	0.02 max
Carbon residue % (mol/mol)	0.20	0.04	0.04	0.03	0.05 max	0.30 max
Copper strip corrosion test (3h, 50ºC)	4	3	1	2	No.3 max	1
Distillation temperature 90% ºC	383	355	-	-	360 max	

Table 2. Glycerine contents

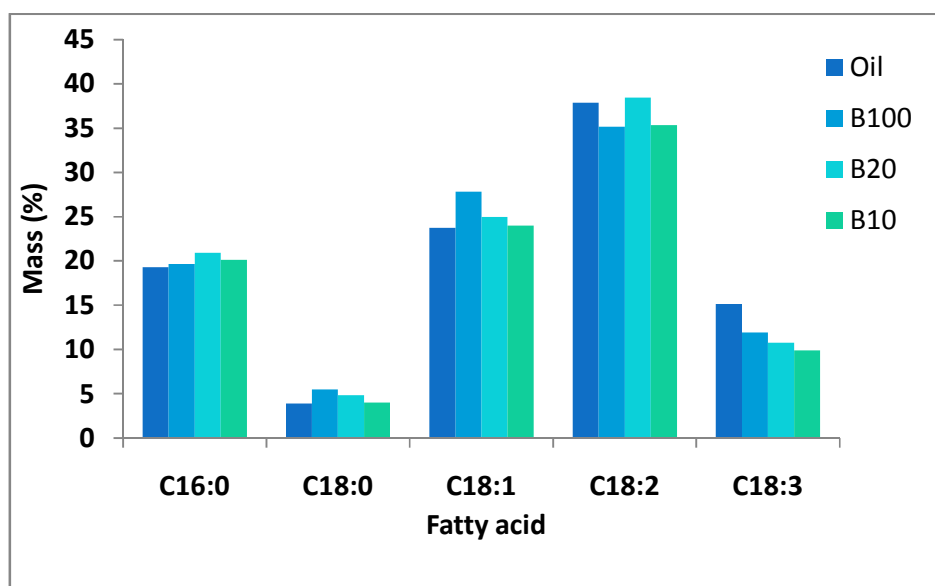| Compound	Rubber seed oil	B100	B10	B20	ASTM D6751-02	EN 14214
Methanol content % (mol/mol)	0.001	0.128	0.015	0.026		**0.20 max**
Free glycerine % (mol/mol)	0.98	0.019	0.003	0.005	0.020	**0.02**
Monoglycerine % (mol/mol)	0.003	0.191	0.006	0.015		**0.80**
Diglycerine % (mol/mol)	0.002	0.015	0.002	0.004		**0.20**
Triglyceride % (mol/mol)	98.755	0.006	0.001	0.007		**0.20**
Total glycerine % (mol/mol)	99.74	0.231	0.056	0.032	0.240	**0.25**

Fig. 1. Fatty acid profile of RSO, B100, B20 and B10

The cloud point is the temperature when wax would start to appear when cooled while the pour point is the temperature at which the wax would be enough to cause the fuel to solidify and no longer flow. Cold filter plugging point is when the fuel has solidified and blocks flow through the filter.

The cloud point of the oil was 25°C and reduced to 9°C for the B100, 8°C for B10 and 1°C for B20. The pour point for the oil was 18°C. It decreased to 7°C for B100, 5°C for B10 and 9°C for B20. The cold filter plug point for the oil was 22°C, 8°C for B100, 6°C for B10 and 10°C for B20. How biodiesel behaves at low temperature is determined to a large extent by the molecular structure and the degree of unsaturation, as long chain saturated fatty acids tend to have poor cold flow properties (12). The maximum cloud point temperature was 9°C, the pour point was 7°C while the cold filter plugging point was 8°C. These values are above the zero degree hence the fuel cannot be used where the temperature can fall below the freezing point.

3.4 Flash Point

Flash point is the lowest temperature at which the fumes above the surface of a heated fuel will flash momentarily when a standard source of flame is placed above it. The test provides a yardstick for estimating how easily a fuel will burn and hence how safe a fuel is in use and storage. The flash point of biodiesel are usually higher that of diesel because of the oxygen content. The flash point for RSO of 165°C reduced to 141°C for B100 while the values for B10 and B20 were 83°C and 91°C respectively, and which although are within the limits for biodiesel are higher than that for diesel fuel. High flash point means that the fuel will ignite at a much higher temperature, thus preventing spontaneous ignition that is responsible for the characteristic diesel knock and allow the fuel to burn for a much longer duration which will ensure more complete combustion and hence lower amount of pollutants in the exhaust gases.

3.5 Viscosity

Dynamic viscosity is the tangential force per unit area of either of two parallel planes within the sample at unit distance apart when one plane moves with unit relative velocity in its own plane. Kinematic viscosity is the dynamic viscosity/ relative density.

RSO has dynamic and kinematic viscosities of 67.72 mN s/m^2 and 74.31 mm^2/s respectively. The kinematic viscosity for B100 is outside the limits while those of the blends are outside the limits for biodiesel. Viscosity test is of primary importance for biodiesel because the operation of fuel injection equipment depends on the viscosity, especially at low temperatures when the high viscosity can affects the flow of fuel or can even leak when the temperature is high and the oil become too thin. Dynamic viscosity is of

interest in relation to the settling rates of contaminants, and kinematic viscosity in respect of pumping and atomization [29].

3.6 Heating Values

RSO has higher and lower heating values 40.20 MJ/kg and 37.10 MJ/kg while for B100 they were 37.3 MJ/kg and 40.3 MJ/kg respectively. These values are slightly lower than the value for diesel fuel which is consistent with the trend for biodiesel. The heating values increased after transesterification and they are also raised when blended with diesel because diesel has higher heating values. It has been reported [28],[29] that the lower heating value of vegetable oils varies with the composition of the fatty acids and where they were grown.

3.7 Calculated Cetane Index

Cetane index (CI) is a measure of how quick diesel fuels burns upon injection into the cylinder and hence the quality of the fuel. It influences the ignition delay from the time the fuel is injected to the commencement of combustion. High CI promotes ease of starting, amount of exhaust emissions, smoothness of driving before the engine warms up, diesel knock and vibration of engine structures. Biodiesel generally have higher cetane index than diesel fuel as a result of the oxygen content [20]. The feed stock also affects the CI because some of the constituent fatty acids have CI of up to 100. CI of biodiesel also depends to a large extent on how the fatty

acids are distributed [28] and highly saturated and long fatty acid chain feedstock have high cetane index. The variation of CI with blending of biodiesel with diesel is linear [30,31] and blending equations have been developed to predict the CI of biodiesel from their properties [32].

The cetane index of RSO and B100 are 46.3 and 51 respectively but it reduced to 45.3 for B10 and 46.01 for B20 and this can be seen in Fig. 2. The CI for B100 is above the minimum limit for biodiesel but after blending it reduced because of the lower cetane index of diesel.

3.8 Water Content and Sediments

This test is used for the determination of the volume of free water and sediment in the fuels hence in a way, a measure of cleanliness of the fuel. In the transesterification of vegetable oil with alkaline catalysts, it has been stressed that water can inhibit the process [33,34] and has to be limited. Free water promotes microbial growth, free fatty acid and the resultant sludge and slime formed can cause blockage of fuel filters and fuel lines causing reduction of lubrication. Sediments when present in the fuel, can also plug fuel filters and contribute to the formation of deposits on fuel injectors and other engine parts. RSO contains 13% water by volume, which fell drastically after transesterification and drying. The moisture content was also very high but decreased substantially after transesterification.
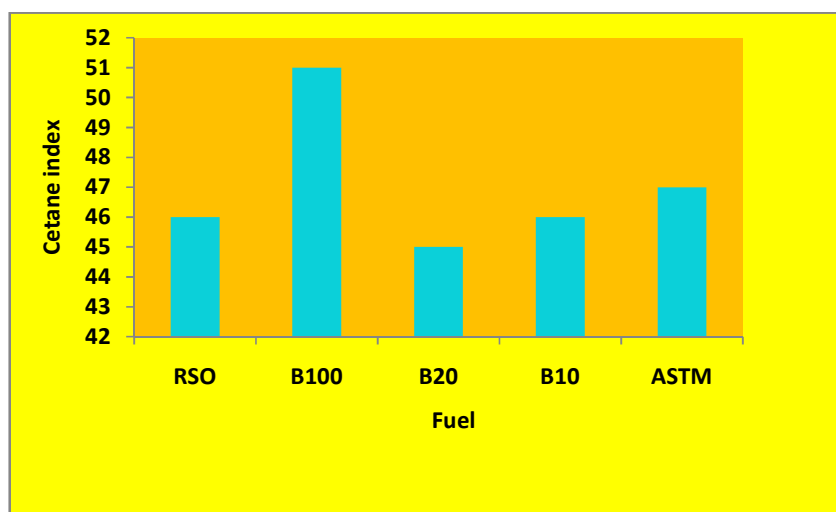

Fig. 2. Cetane index of fuels

3.9 Cold Soak Filtration

The cold soak filtration is 320ºC for RSO and falls to 264, 81 and 98ºC for the B100 and the B10 and B20 blends respectively. Biodiesel contains waxes and water that can precipitate in cold temperature along with glycerin and sterol glycosides to form particulate matters which can block oil filters. These should be removed before use and filters should be designed so that they can store accumulated water and allow it to be drained off without removing the filter.

3.10 Iodine Values

The Iodine value of a fuel is an indicator of the degree of unsaturation and drying quality. Unsaturation can result into excessive carbon deposits in the combustion chamber and create storage stability problems. High values can lead to polymerization of the fuel and formation of excessive deposits in the engine.

The iodine values for the samples are all below the limits for biodiesel. The iodine value for B100 is 4.6% higher than the 101.1 gl$_2$/100g obtained for the B100 by [13], [35]. The iodine values are all below the maximum for biodiesel and reduced further with blending.

3.11 Peroxide Value

This is an indicator of oil self ignition property and high value is an evidence of high degree of rancidity and fuel oxidation [36]. A peroxide value of 29.0 gl$_2$/100g for the biodiesel is high compared to common vegetable oils. Blending tends to stabilize the peroxide value of the biodiesel.

3.12 Oxidation Stability

Transesterification is a reversible reaction that continues over a long period especially if the initial reaction was incomplete. During this period, any remaining double bonds are broken and are readily reactive with oxygen. Oxidation products are mostly soluble in the fuel and are acidic. They can lead to the formation of insoluble sediments and gums, which can increase viscosity, plug filter and lead to deposits within the injection system and the combustion chamber and in fuel tanks [37]. Because they are acidic, they can cause corrosion and react with engine oil to form gum, sludge and vanish

which deteriorates the oil. The oxidative stability of RSO measured at 110ºC was 17 hr, after transesterification it reduced to 8 hours, after blending it was 0.8 for B10 and 1.5 hours for B20. Transesterification lowered the oxidative stability while blending increased it but all the values are higher than for diesel.

3.13 Acid Number and Free Fatty Acid

Acid number is the amount of base needed to titrate a sample to a specified end point. It is a measure of the amount of fatty acid that has been liberated in a biodiesel. Too much free fatty acid in the fuel can promote corrosive activities and may also be a sign of water in the fuel, incomplete transesterification or high oxidative degradation. Excessive free fatty acid in the oil can promote soap formation, which can retard the transesterification process and hence reduce biodiesel yield. The free fatty acid and acid values of the oil are 23.68 mgKOH/gm and 47.124 mgKOH/gm respectively. The FFA value is close to the 24% obtained by [20] and which is too high for direct alkaline transesterification as it can inhibit the separation of ester and glycerol. As can be seen in Figs. 3 and 4, both the FFA and acid value reduced after transesterification but increased with increasing amount of diesel in the blends.

3.14 Saponification Values

The Saponification value of 183.73 for the oil is within the range for most vegetable oils [38,39] hence, it would also be suitable for the production of soap and shampoo. Moderate amount of soap in biodiesel can help reduce friction between moving parts and improve cleanliness in the fuel pump.

3.15 Soap Content

The soap content for RSO was zero but increased to 8 for B100 as a result of using sodium hydroxide for the transesterification process but reduced with blending. Soap content is a measure of the effectiveness of the washing process after transesterification. Its presence can affect the operation of fuel pump where it helps in lubricating moving parts and cleansing the system. High content of soap in biodiesel was observed to cause excessive smoke and had adverse effects on the combustion process.
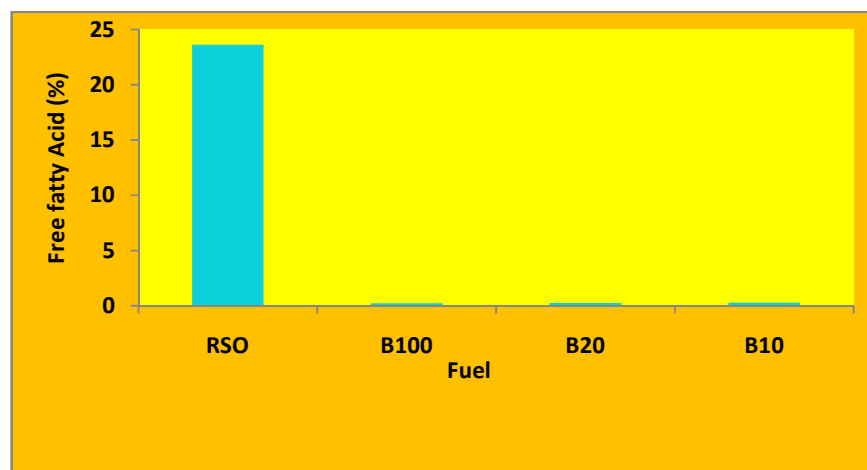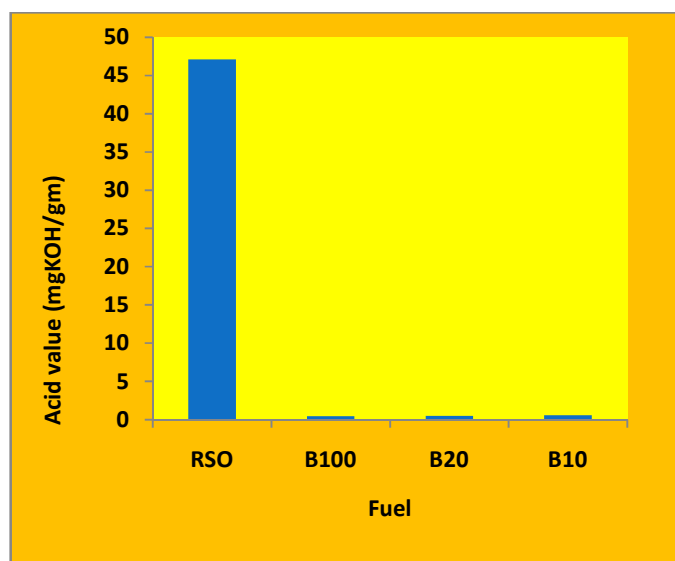
Fig. 3. Free fatty acid

Fig. 4. Acid value

3.16 PH Value

The pH value is a measure of the alkalinity and the amount of fatty acids in the fuel. The value of 7 in the result indicates that they are alkaline and the alkalinity increased with blending.

3.17 Refractive Index

The results obtained shows that refractive index of the oil was 1.47, which reduced to 1.34 after transesterification but increased again after blending with diesel to 1.48 due to the diluting effect of the diesel. Refractive index is a measure of the cleanliness, uniformity and the presence of high molecular mass components in the fuel [40].

3.18 Carbon Residue

The carbon residue test gives the remaining part when a sample of biodiesel has been subjected to thermal decomposition and hence an indication of coking tendency of the fuel. It involves heating the fuel to a high temperature in the absence of oxygen to simulate highly simplified burning conditions in an engine. Most of the volatile parts of the fuel will vaporize and be driven off but a portion may decompose and pyrolize to hard carbonaceous deposits. This is particularly important in diesel engine because of the possibility of carbon residue clogging the fuel injector's orifices and being deposited on piston and combustion chamber. The most common

cause of excessive carbon residue in biodiesel is the excessive level of total glycerin, soaps and other organic impurities. The carbon residue was 0.04 (mol/mol) and below the maximum ASTM limits. Other values are as shown in Fig. 5.

3.19 Sulfated Ash

This is the alkaline catalyst residue remaining after a fuel sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to a constant weight.

This test is a measure of the metallic elements remaining in the ash residue after the fuel has been burned. The test is essential for biodiesel as it gives the amount of the metallic elements in the ash that also originated from the catalyst used for the transesterification process. The sodium and potassium commonly used for transesterification have low melting points and may cause engine damage in combustion chamber and cause injector deposits. The sulfated ash for B100 was 0.03% (mol/mol) as shown in Fig. 5, which is higher than the 0.02% ASTM maximum limits.

3.20 Total Glycerol

Triglyceride consists of three fatty acids bonded to one glycerol molecule, each by an ester

linkage. The transesterification process goes through three successive stages during which mono-, di- and triglycerides are formed. Total glycerol is the sum of the concentrations of free glycerol and glycerol bound in the form of mono-, di- and triglycerides. The concentration of the various components depends on the production process. Fuels out of specifications with respect to these parameters are prone to coking and may thus cause the formation of deposits on fuel pumps, injector nozzles, pistons and valves [36]. Total glycerol affects storage stability which is a measure of how well the quality of fuel will be maintained in storage when in contact with air and water. Mono- and di- glycerides are intermediate and unstable components which, if present in biodiesel can form gums and sediments. When in contact with air can cause filter clogging, combustion chamber deposits, and gumming of the injection system components, as well as increased engine wear. The methanol and other by-products of the transesterification process are all within the ASTM and EN limits as shown in Table 2. The high triglyceride value is a reflection of the completeness of the transesterification reaction.
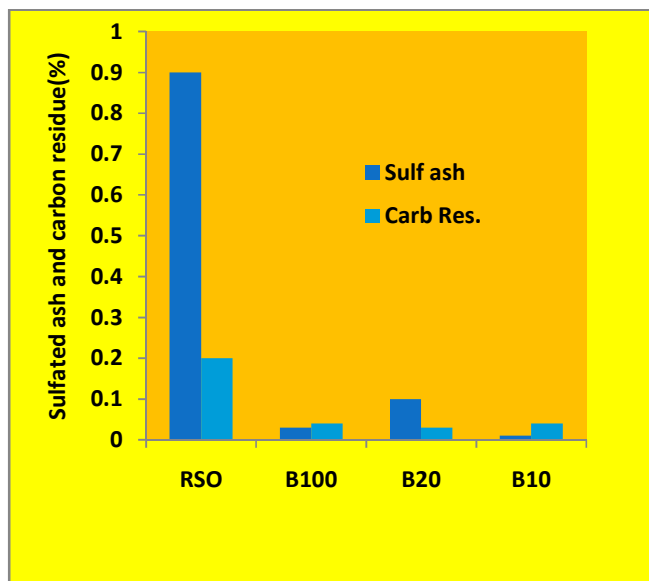
Fig. 5. Sulfated ash and carbon residue

3.21 Distillation Temperature, 90% Recovered, Maximum

This parameter is an important tool for determining the presence of other substances and in some cases meeting the legal definition of biodiesel (i.e. monoalkyl esters). The vacuum distillation end point is below the 360ºC maximum at 90% distillation of EN D1160. The distillation temperature increased with the amount of biodiesel in the blend, the phenomenon has been reported by [31]. The distillation curves for the RSO and B100 are shown in Fig. 6. The two distillation curves are similar in trend but the initial boiling point for biodiesel is 210ºC as against 280ºC for the RSO, thus the B100 will start to boil 70ºC before the RSO and would completely evaporate 40ºC before the oil does. B100 hence contains more volatile components, which can affect the injection timing, ease of starting, combustion characteristics, evaporative losses, lubricating oil dilution and exhaust emissions. It was reported by [34] that the increase in the ignition delay and the more fuel release at the beginning of the combustion is responsible for the characteristic high combustion temperature of biodiesel that is responsible for increased level of NO_X in exhaust gases. The effect of blending is to lower the boiling temperature and move the distillation characteristic towards that of diesel.

3.22 Metal Components

The metallic components in the fuel originate from natural sources. They constitute impurities in the fuel which are deposited on engine components after combustion. Despite not participating in the combustion processes, they react with components made from metals and are also deposited on pistons, valves, injectors, combustion chamber and exhaust systems and must hence be limited to recommended values. The values of metallic elements are high for the oil but reduced to within limits in B100 showing that they have been absorbed in the glycerol. The test results are shown in Table 3.

3.23 Sulphur

The sulphur content was very high but soon fell within limits for the B100 but increases again with blending as the diesel used contained sulphur. The sulphur content of the B100 was 6.40 ppm and lower than the maximum specified by EN and 32.00 ppm for diesel. Sulphur can affect catalytic converter effectiveness and the SO_2 produced in the exhaust emission can increase atmospheric pollution, cause acid rain and promote soiling.

3.24 Phosphorus Content

The origin of phosphorus is from the phospholipids in the oil. Phosphorus can adversely affect the effectiveness of exhaust emission catalytic systems after some time [35]. The value for the biodiesel of 8 mg/kg is less than the maximum of 10 mg/kg specified by EN standard.

Table 3. Metal components

| Material	Detection Limit (ppm)	Spike recovery	RSO	B100	B20	B10	ASTM D6751-02	EU 14214
Sodium Na 589.592r	0.0193 80	100.9	8.90	1.80	0.04	0.04		5.0 max
Potassium K766.491r	0.070 40	101.1	4.2	1.00	0.09	0.05		5.0 max
Calcium Ca317.933	0.0029 2	101.6	4.70	0.35	0.08	0.04		5.0 max
Magnesium Mg285.213r	0.0009 0.20	99.1	1.80	0.60	0.12	0.06		5.0 max
Phosphorous P212.618r	0.0227 5	99.1	8.00	2.80	7.00	3.50	0.001	10.0 max
Sulphur S180.731r	0.114 15	98.7	23.50	6.40	26.90	29.60	0.05 max	10.0 max
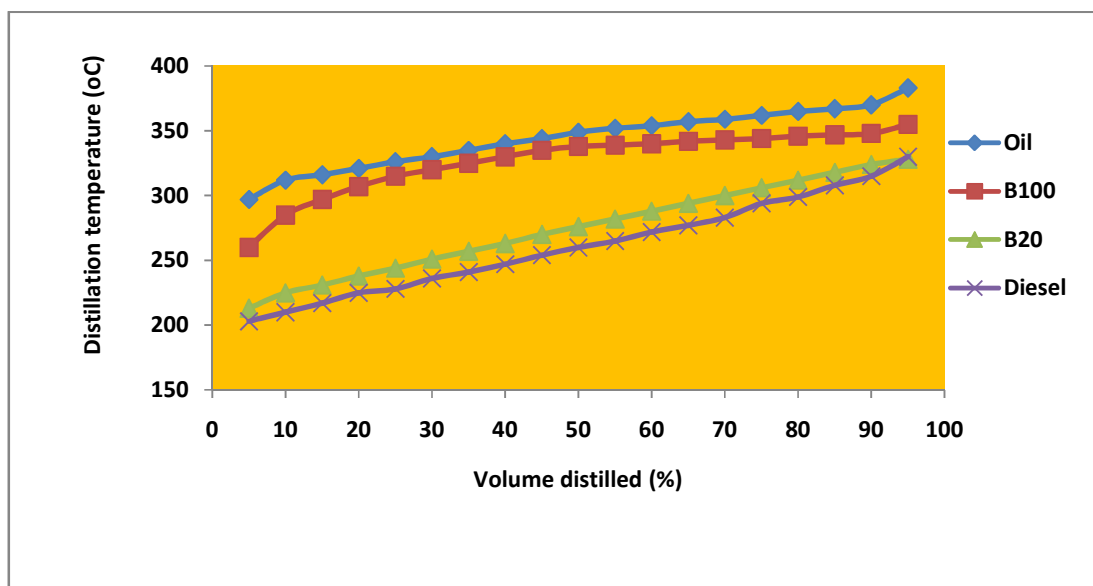
Fig. 6. Distillation curves for rubber seed oil, B100 and B20 and diesel

4. CONCLUSION

Rubber seed oil biodiesel contains 23.74% of oleic, 37.9% of linoleic, 15.16% of linolenic, 19.32% of palmitic, 3.876% of stearic acids and 76.80% of unsaturated ones. The oil is very sensitive to heat and turns to latex above 110ºC. It has an oil content of 40%. The oil is highly corrosive while the B100 is as corrosive as diesel. Radical changes in properties occurred after transesterification and most of the properties of the B100, B20 and B10 are within the ASTM and EN limits for biodiesel. Blending has a tendency to shift the properties towards those of diesel and they increase or decrease linearly. The carbon residue is within limits but sulfated ash had to be blended to bring it to within limits. Based on the properties and fatty acid profile, the fuel would be suitable for use as alternative fuel for diesel engines.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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