

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

Abstract

Many oil sources for biodiesel production in African have not been well researched resulting in scanty information about them. To overcome this problem, 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 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 shows 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.

Key words: Rubber seed oil, fatty acid profile, characterization, biodiesel, blend.

List of abbreviations. ASTM: American Society for Test and Materials, AOSC: American Oil chemist Society, EU: European Union

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) and (10%) B10 and (20%) B20 blends with diesel, which is the ratio that gives the nearest property to diesel. Biodiesel has been defined as the mono alkyl esters of vegetable oil and animal fats [6]. It has superior fuel properties to diesel fuel in many respects, biodegradable, environment friendly, nontoxic, renewable, lower harmful exhaust emission and safer than diesel [7], [8], [9], [10] and [11]. The fuel properties of biodiesels are to a large extent dependent on feed stocks, which vary not only with specy but also where grown and method of production [12]. The fuel standards for biodiesel, which evolved from diesel standards, is to ensure quality assurance irrespective of feedstock, by limiting the amount of impurities such as triglycerides, monoglycerides, diglycerides, water, free fatty acid, soap and residual alcohol in the fuel. These materials need to be limited in biodiesel because 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 35°C which, reduce 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 60°C. The residual n-hexane in the oil was removed in a vacuum rotary evaporator operated at 75°C. The oil obtained was weighed and the percentage oil yield was calculated by 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 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] and [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 anhydrous methanol at a molar ratio of 4 to 1 and 3 g/litre of sodium hydroxide as catalyst. The processor was stirred at 60 °C, and 600 rpm for 5 hours, after which the mixture was poured into a decanter and allowed to settle for overnight for the reaction to reach equilibrium and separate into biodiesel and glycerol. The biodiesel was next washed as described [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 at 60 °C

2.5. Determination of Fuel and Physicochemical Properties

The fuel and physicochemical properties of the rubber seed oil, its 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 45°C was cooled in Herzog HCP852 at specified rate. Checks were made at intervals of 3°C record when 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 the Brookfield equipment model LV-DVII, coupled to a heat controller at a temperature of 30°C, using a small sample adaptor while the kinematic viscosity was determined with a Herzog GmbH MP - 480 that involves measuring the time for a fixed volume of the fuel to flow under gravity through a capillary at a constant temperature.

$$\text{Kinematic viscosity} = \frac{\text{calibration constant (mm}^2/\text{s}^2\text{)}}{\text{Mean time of flow (s)}}$$

2.5.5. Flash Point

Flash point measurements were done according using Kehler Model K-16270 (Pensky-Martens Closed Flash Tester) flash point apparatus to ASTM D6751.

2.5.6. Heating Values

The lower heating value was measured using the oxygen bomb calorimeter (Parr Instrument Company, US.) following the ASTM D240 method.

2.5.7. Cetane Index

The cetane indices of the oil, biodiesel and blends were calculated using equation 2 [24].

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

2.

where G is the API (American Petroleum Institute) specific gravity and 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 with 0.01 N sodium thiosulfate for 0.001269 the mixture of tested fuel and chemical reagents until they were light blue and light yellow, respectively following the method of AOCS cd8, 1980.

The values were calculated by equations (3), (4) and (5) respectively as follows:

$$\text{Iodine value} = \frac{(B - T) \times C \times 0.001269}{Y} \quad (3)$$

$$\text{Peroxide value} = \frac{(T - B) \times C \times 1000}{Y} \quad (4)$$

$$\text{Saponification value} = \frac{(B - T) \times 28.5}{Y} \quad (5)$$

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 number was determined by titrating with 0.01 N potassium hydroxide for the mixture of tested fuel and chemical reagents until the appearance of the color pink. The acid value (mgKOH/g) was determined to ASTM D664 using equation 6

$$\text{Acid Number} = \frac{56.1V \times C}{Y} \quad (6)$$

Where V = Volume of KOH used for titration (mL), C = Concentration of KOH used for titration (mol/L) and Y = mass of sample used for analysis (g).

2.5.10. Oxidative Stability

A glass ware apparatus for ASTM D 2274 was used for the oxidation stability test. The fuel was made to degrade by heating and oxygenating the sample in a shorter period of induction time. Oxygen was bubbled for 16 hours while the fuel was held at 95 °C. Thereafter, the fuel sample was filtered to measure the amount of any insoluble that was formed. Finally, the amount of time that the fuel could be stored before deterioration by forming acids was then 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 4 °C 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 20 °C 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 20 °C.

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 was determined by heating a sample to 500 °C in nitrogen filled chamber at controlled rate to ensure that the sample cokes and does not combust. The formed volatile compounds were flushed from the chamber by nitrogen, and the mass of the remaining coke determined. The test is designed to simulate the formation of carbon deposits in the engine by the fuel.

2.5.16. Sulfated Ash

Isotemp muffle furnace was used for ash analysis. The residue was allowed to cool down and there after treated with sulfuric acid and heated to 750 °C until oxidation of carbon was complete. The ash was then cooled, retreated with sulfuric acid and heated to 750 °C to constant weight. To obtain the sulfated ash content of the samples, the final weight was divided by the initial weight and then multiplied by 100 to express as percentage.

2.5.17. Water and Sediment

Water and sediment content were obtained by centrifuge model HNS II (Thermo Electron corp,

US). 100 ml of each sample was poured into a centrifuge tube and spun at 800 rev/min for 10 minutes. After centrifugation, the volume of water and sediment which settled into the tip of the centrifuge tube was read to the nearest 0.005 ml and recorded as the volumetric 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 prepared by diluting 1:10 with kerosine. The dilution is to eliminate possible viscosity effects that may affect accuracy. The analyzer was calibrated with standards prepared by diluting pure biodiesel stock standards. The standard concentrations were 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 entitled “Total, free and combined glycerol Iodometric-periodic Acid method as well as methanol Content” was used. 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 at between 1 kpa and 83 kPa. The uncertainty was less than 1 °C 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

Copper strip corrosion test was conducted according to ASTM D130 protocol as reported in (13). A polish copper strip was immersed in 50 ml sample of the oil and methyl ester for 3 hours at 50°C. At the expiration of the duration each strip was washed in a standard solvent and the result were compared with standard description of tarnished and corrosion. This test is important because many parts of fuel injector system and fuel tank are made from copper or copper alloys.

3.0 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 110°C. The implication is that B100 cannot be effectively dried by heating. The oil content was 40.4%. All the discussion refer to the results shown in Tables 1, 2 and 3.

3.1. Fatty Acid Profile

The fatty acid profile of RSO, B100 and B20 are shown in Figure.1 The oil contains 19% palmitic and 3.876 % stearic acids both of which are saturated, and 23.7% oleic, 37.7% linoleic and 15% linolenic acids. Making it 76.8% unsaturated. The profile for the methyl ester 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/m³ which reduced to 877 kg/m³ for B100, 855 kg/m³ for B20 and 857.7 kg/m³ 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/m³ for biodiesel will increase the viscosity from 2.59 to 4.63 mm²/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

Cold temperature behavior of biodiesel is an important quality criterion, as frozen fuel may cause blockage of the fuel lines and filters thereby starving the engine of fuel. The two most important criteria are the cloud and pour points. Cloud point is the temperature at which wax first becomes visible when the fuel is cooled while Pour Point 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. 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 increased to °C 7for 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. The cold point characteristics of biodiesel products depend on chain length and degrees of unsaturation, with long chain saturated fatty acid esters displaying particularly unfavorable cold temperature behavior [12]. The maximum cloud, pour and cold filter plugging points are 9,7,8 °C respectively and are all above zero, which limits their applications in cold regions. The oil has adverse cold flow properties making it unsuitable as a fuel but not as feedstock for tyre production.

3.4. Flash Point

This is the lowest temperature to a barometric pressure of 101.3 kPa at which a liquid sample produces sufficient vapor for the air-vapor mixture above the surface to flash momentarily on exposure to a standard source of ignition. It is a measure of how easily a fuel burns and thus an important safety criterion in transport and storage. The flash points of pure biodiesels are usually higher than the ASTM limits because of the oxygen content that supports combustion, but fall rapidly with increasing amount of diesel in the blend. RSO has a flash point of 165 °C, the value for B100 is 141°C while the values for B10 and B20 are 83 °C and 91 °C respectively and which although are below the minimum 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. The dynamic and kinematic viscosities of the RSO are 67.72 and 74.31 mm²/s respectively. Those of B100 are just outside the limits while those of the blends are below the limits for biodiesel. Viscosity is an important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel or leakage at high temperature when 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

The higher and lower heating values for RSO are 40.20 MJ/kg and 37.10 MJ/kg, for B100 are 37.3 MJ/kg and 40.3 MJ/kg respectively and are slightly less than that of diesel fuel which is consistent with the trend for biodiesel. The heating values increases after transesterification and with the amount of diesel in the blend because diesel has higher heating values. The lower heating value of vegetable oils depends on the composition of the fatty acids, where grown and its vintage among other factors [28]. It increases if the length of the fatty acids increases, and does so to an even greater extent if the content of oxygen in the oil decreases [29]. However, [28] reported that it decreases as the volume of double bond increases.

3.7. Calculated Cetane Index.

This is a measure of the ignition quality of diesel fuels and one of the prime indicators of the quality of diesel fuel. It affects the ignition delay time of a fuel upon injection into the combustion chamber, it influences ease of starting, duration of white smoke after start up, drivability before warm up and intensity of diesel knock at idle and vibration of engine structures. Biodiesels usually have a higher cetane index than diesel fuel because of its oxygen content [30] and also because some of the fatty acids present in the fuel have very high octane number. It has been shown [28] that the cetane index of biodiesel depends essentially on the distribution of fatty acids in the feedstock. The longer the fatty acid carbon chains and the more

saturated the molecules, the higher the cetane index. The effect of blending biodiesel on cetane index is almost linear for mixtures of esters with diesel fuels [30,31]. It has been reported [32] that it is possible to determine the cetane index of esters from their physical properties and equations were developed for predicting the cetane index of esters from their properties. The calculated cetane index of the RSO of 46.3 increased to 51 for the B100 45.3 and 46.01 for B10 and B20 respectively as shown in Figure 2. That of B100 is above the minimum limit for biodiesel but reduces with blending because diesel has lower cetane index.

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 course reduction of lubrication . Sediments when present in the fuel, may 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 because of the drying after treatment. The moisture content was also very high but decreased substantially after transesterification.

3.9. Cold Soak Filtration

The cold soak filtration is 320 °C for RSO and falls to 264, 81 and 98 °C 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

Iodine number is a measure of the total unsaturation within a mixture of fatty acids, and is expressed in grams of iodine which react with 100 grams of biodiesel. Unsaturation can lead to deposit formation and storage stability problems with biodiesel. Fuels with higher iodine number

tend to polymerize and form deposits on injector nozzles, combustion chamber, valves and piston after combustion. The iodine values for the RSO, B100, B10 and B20 are below the maximum for biodiesel. The value for ROSME of 106 obtained is less than the 101.1 gI₂/100g obtained for B100 by [13,35]. The iodine values are all below the maximum for biodiesel and reduced further with blending. Iodine value is an indication of the drying quality of an oil.

3.11. Peroxide Value

This is an indicator of oil autoignition and high value is an indication of high degree of rancidity and fuel oxidation [36]. A peroxide value of 29.0 gI₂/100g 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 acidic and 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 varnish which deteriorates the oil. The oxidative stability of RSO at 110 °C was 17 hr, 8 hours for B100, 0.8 and 1.5 hours for B10 and B20 respectively. It reduces after transesterification but increases with blending and in all cases higher than diesel.

3.13. Acid Number and Free Fatty Acid

Acid number is the quantity of base required to titrate a sample to a specified end point. It is a measure of the quantity of fatty acid that has been broken free in biodiesel. Excessive free fatty acid in the fuel can be corrosive and may be a symptom of water in the fuel, poor production or

oxidative degradation. Excessive free fatty acid in the oil can lead to soap formation and inhibit the transesterification process thus reducing 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 Figure 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 they help in lubricating moving parts and cleansing the system. High content of soap in biodiesel has been observed to cause excessive smoke and adversely affect the combustion process.

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 refractive index was 1.47 and reduced to 1.34 after transesterification but increases to 1.48 after blending due to the diluting effect of the diesel added. 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 pyrolyze to hard carbonaceous deposits. This is particularly important in diesel engine because of the possibility of carbon residue clogging the fuel injectors and 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 Figure 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. It is a measure of the mineral ash residue when a fuel is burned and contains most of the metals in the fuel. It is an important test for biodiesel because it indicates the quantity of residue metals in the fuel that came from the catalyst used in 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 Figure 5 and 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 3. The high triglyceride value is a reflection of the completeness of the transesterification reaction.

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 360°C 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 Figure 1. The two distillation curves are similar in trend but the initial boiling point for biodiesel is 210°C as against 280°C for the RSO, thus the B100 will start to boil 70°C before the RSO and would completely evaporate 40°C 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

Metal components in the fuel originate from natural sources. They constitute impurities in the fuel which are deposited on engine components after combustion. They also react with metallic components of fuel systems and should be limited to recommended values to reduce deposits on engine components, injectors and catalytic system. Values for all the rare earth metals are high for the oil but below the limits for biodiesel for B100 showing that they have been absorbed in the glycerol. The 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 is 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 SO₂ 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.

4.0 Conclusions

Rubber seed oil Biodiesel contains 23.74% oleic, 37.9% linoleic, 15.16% linolenic, 19.32% palmitic %, 3.876 % stearic acids and 76.80% unsaturated. The oil is very sensitive to heat and turns to latex above 110°C. 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.

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Table 1. Properties of Rubber Seed Oil, its Ester and Blends to ASTM D6751-02 and EN 14214

Property	Rubber Seed Oil	B100	B10	B20	ASTM D6751-02	EN 14214
Density kg/m ³ at 15 °C	910	877.3	855	857.7		860-900
Relative density kg/m ³ at 15 °C	0.911	0.878	0.856	0.858		
Cloud point °C	25	9	8	1		
Pour point °C	18	7	5	9		
Cold filter Plug Point °C	22	8	6	10		
Flash Point °C	165	141	83	91		120 min
Dynamic Viscosity (mN s/m ²) at 40°C	67.72	5.07	2.53	2.84		
Kinematic Viscosity (mm ² /s) at 40°C	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) 110°C	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 °C	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 15 °C	1.467	1.343	1.480	1.408		
Sulfated ash %	0.90	0.03	0.01	0.01	0.02 max	0.02 max

(mol/mol)						
Carbon residue % (mol/mol)	0.20	0.04	0.04	0.03	0.05 max	0.30 max
Copper Strip Corrosion Test (3h, 50°C)	4	3	1	2	No.3 max	1
Distillation temperature 90% °C	383	355	-	-	360 max	

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564 **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

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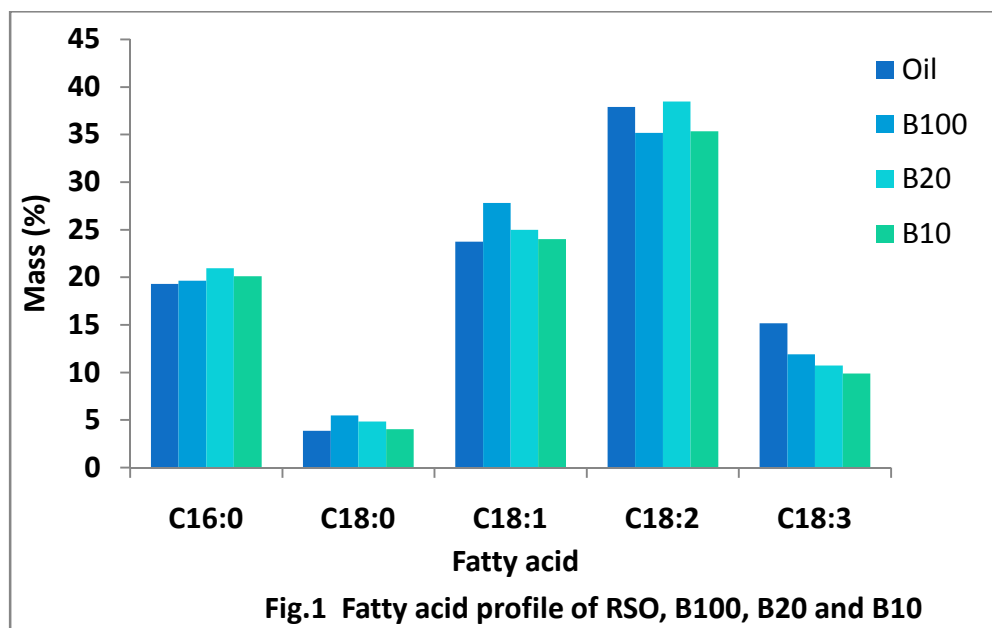
566 **Table 3. Metal contents (ppm).**

Material	Detection	Spike	RSO	B100	B20	B10	ASTM	EU
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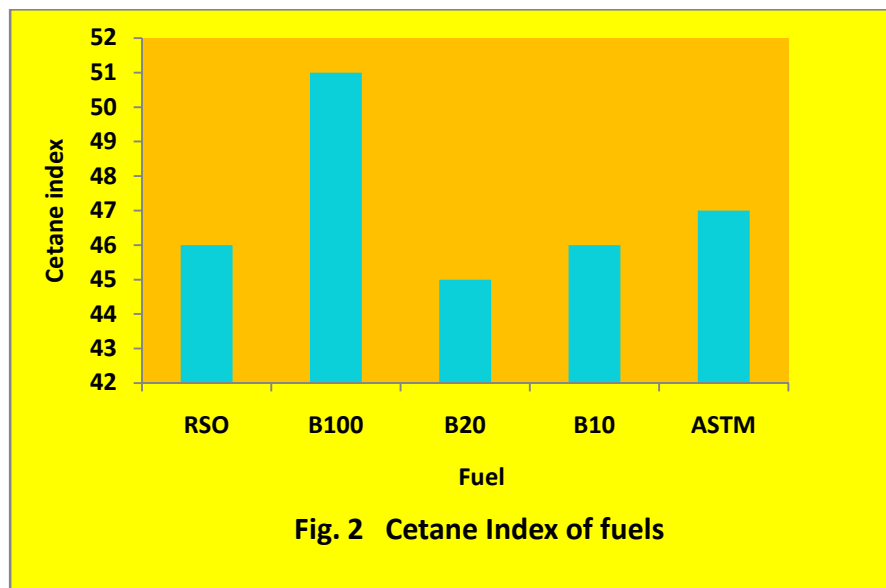
	Limit (ppm)	recovery					D6751-02	14214
Sodium Na 589.592r	0.0193 80	100.9	8.90	1.80	0.04	0.04		5.0 max
Potassium K766.491r	0.070 40	101.1	4.2	1.00	0.09	0.05		5.0 max
Calcium Ca317.933	0.0029 2	101.6	4.70	0.35	0.08	0.04		5.0 max
Magnesium Mg285.213r	0.0009 0.20	99.1	1.80	0.60	0.12	0.06		5.0 max
Phosphorous 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

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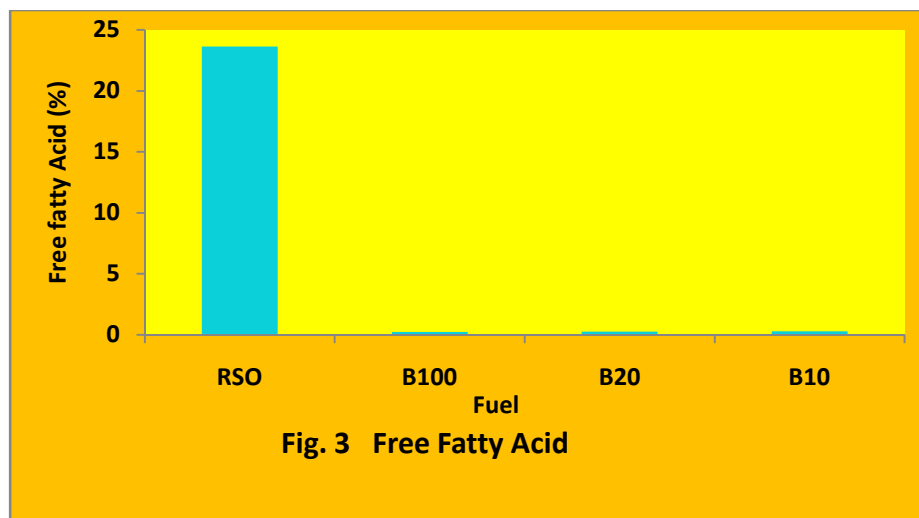


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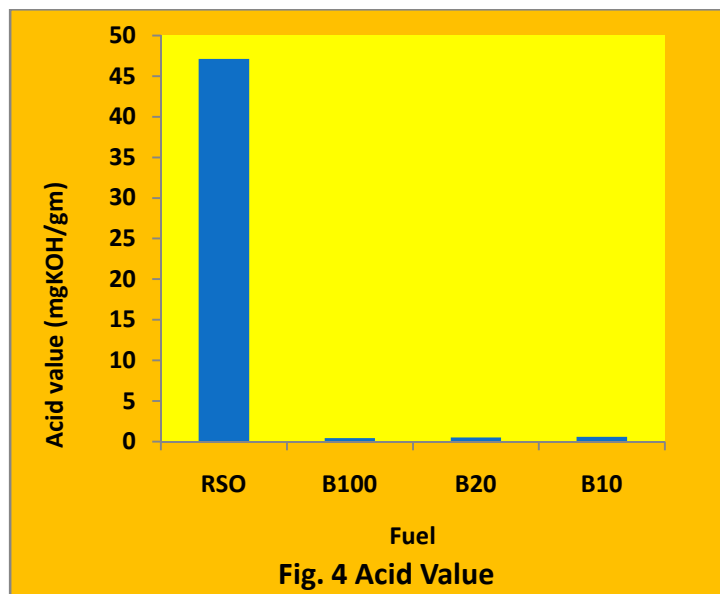
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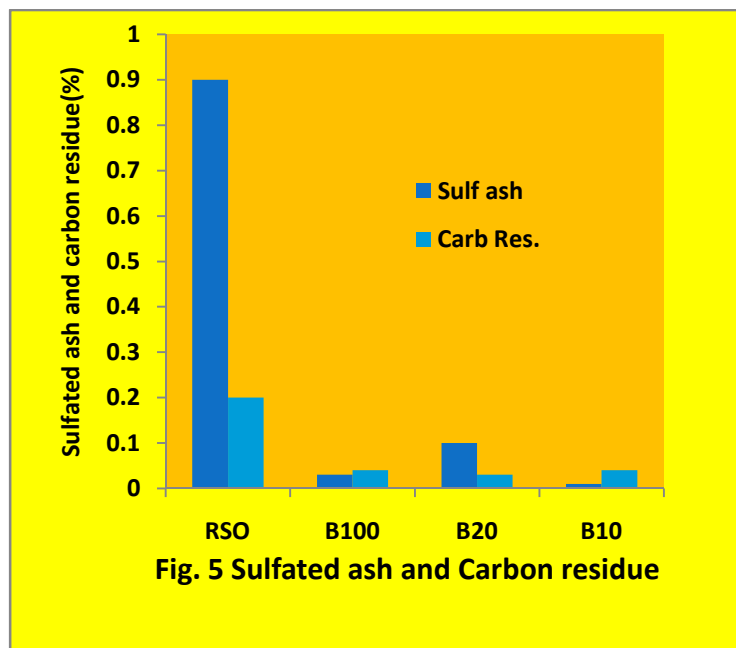
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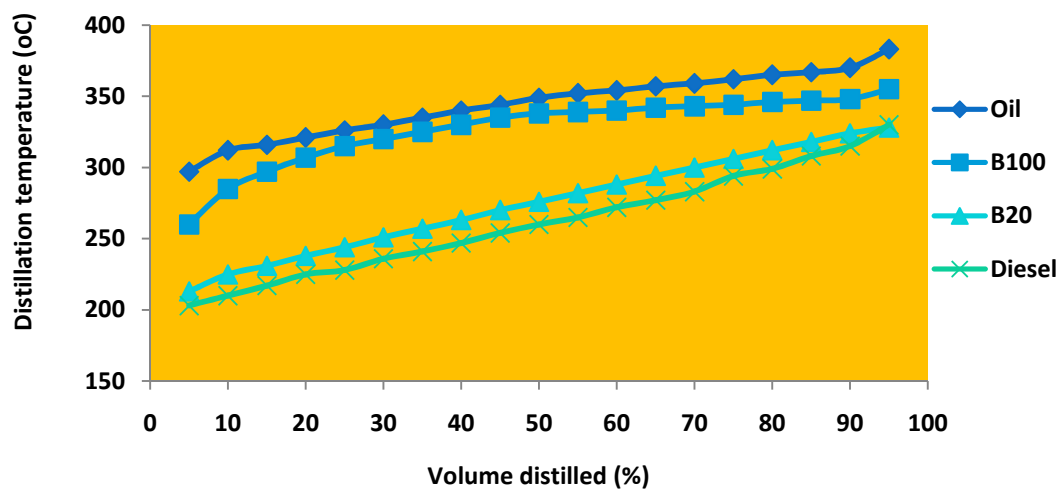


Fig.6 Distillation Curves for Rubber seed Oil, B100 and B20 and diesel