

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

Emmanuel I. Bello and Francis Otu

Department of Mechanical Engineering, The Federal University of Technology, Akure, Nigeria.

Author's Contributions

The work was carried out by both Authors.

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 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.

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, 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 35°C, 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 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 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 (H₂SO₄) 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 methanol at a volume ratio of 4 to 1 and sodium

hydroxide as catalyst at 3g/litre. The reactor was stirred continuously for 5 hours at 600 rev/min, and a constant temperature of 60°C at the end of which it was poured into a separating funnel and stored overnight for the reaction to reach equilibrium and separate into biodiesel and glycerol. The biodiesel was next 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 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 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 30°C 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).

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

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.

Heating Values

2.5.6. 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].

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

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 AOCS cd8, 1980 and calculating the values by equations (3), (4) and (5).

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

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

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

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

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

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

2.5.10 Oxidative Stability. The oxidative stability test was conducted in a glass ware apparatus for 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 95 °C. After this duration, the insoluble 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 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 test was conducted by heating the fuel at a controlled rate to 500 °C 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 750°C 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 750°C 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 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

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 60°C. 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 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 110°C. 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 figure.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/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

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. 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 acid 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 than 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 $74.31 \text{ mm}^2/\text{s}$ 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 affect 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 number (CI) is a measure of how quick diesel fuels burn 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, 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 cetane number of up to 100. CI of biodiesel 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 Figure 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 cause reduction of lubrication . Sediments when present 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.

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

The Iodine value of a fuel is an indicator of the degree of unsaturation and drying quality of an oil. 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 gI₂/100g 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 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 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 varnish which deteriorates the oil. The oxidative stability of RSO measured at 110 °C 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 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 it helps in lubricating moving parts and cleansing the system. High content of soap in biodiesel was observed to cause excessive smoke and has adverse effects on 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 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 pyrolyze 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 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.

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 Figure 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.

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 6. 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

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 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% 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 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.

References

1. Abdullah BM, Salimon J Physiochemical Characteristics of Malaysian Rubber (Hevea Brasiliensis) seed oil. Euro J. Sci. Res. 2009;31:437- 445.
2. Nwankwo BA, Aigbekaen, Sagay GA Estimates of Rubber (ev) Seed production in Nigeria. In: Industrial Utilization of Natural Rubber, Seed Latex and Wood. Proceedings of Natural Conference (Ed: Ephraim E. Enabor). Rubb. Res. Inst. of Nigeria pp. 1985;78-87.
3. Ramadhas AS, Jayaraj S., Muraleedharan C. Biodiesel Production From High FFA Rubber Seed Oil. Fuel , 2009;84(4):335-340
4. Ikwuagwu OE, Ononogbu IC, Njoku OU Production Of Biodiesel Using Rubber Seed Oil, Ind. Crops. Prod. 2000; 12(1):57-62.
5. Perera E, Dun PD Rubber Seed Oil For Diesel Engines In: Sri-Lanka. J. Rub. Inst. Sri-Lanka 1990; 70: 11-25
6. NBB Facts on Biodiesel. National Biodiesel Board. Jefferson City, MO, USA. 1997.
7. Ma F, Hanna MA, Biodiesel Production: a Review. Bioresource Technology 1999;70(1):1-15.
8. Canakci M, Van Gerpen J, Biodiesel Production via Acid Catalysis. Transactions of the ASAE, 1999; 42(5): 1203-1210.

473 9. Dorado MP, Arnal JM, Gomex J, Gill A, Lopez FJ, The Effects of a Waste Vegetable Oil
474 Blend with Diesel Fuel on Engine Performance. Transactions of ASAE Vol. 45 2002; (3): 519 –
475 523.

476 10. Van Gerpen JC, Shanks B, Prusko R, Clements, D. and Knothe, G. Biodiesel Production
477 Technology. Contract No. DE-AC36-99-GO10337, National Renewable Energy Laboratory. US
478 Department of Energy. 2004.

479 11. Canakci M, Van Gerpen J. Biodiesel Production From Oils And Fats With High Free Fatty
480 Acids. Transactions of ASAE, 2001; 44 (6): 1429-1436.

481 12. Ramadhas AS, Jayaraj S, Muraleedharan C Characterization and the Effects of Using
482 Rubber Seed Oil as Fuel In The Compression Ignition Engines. Renewable Energy 30 2005; (5):
483 795-803.

484 13. Bello, EI, Akinola, AO, Otu, F, Owoyemi, TJ Fuel and Physicochemical Properties of
485 Cashew (*Anacardium 1 occidentale*) Nut Oil, its Biodiesel and Blends with Diesel. British
486 Journal of Applied Science and Technology 2013; 3(4):1055-1069

487 14. Ebewere RO, Iyayi AF, Hymore FK Considerations of the Extraction Process and Potential
488 Technical Applications of Nigerian Rubber Seed Oil. Int. J. of The Physical Sci. 5 2010; (6):
489 826-831

490 15. Goodrum JW, Kilgo MD. Peanut Extraction Using Compressed Carbon Dioxide. Eng. in
491 Agric. 1986; 8: 265-271.

492 16. Sayyar S, Abidin SS, Yunus R, Muhammed A. Extraction of oil from jatropha seeds-
493 Optimization and kinematics. Am. J. App. Sci. 2008; 6 (7):1390-1395.

494 17. Van Gerpen JV. Biodiesel Processing and Production. Fuel Processing Technology 2005;
495 86 (10): 1097-1107.

496 18. Ghadge SV, Raheman H Process Optimization for Biodiesel Production from Mahua
497 (*Mahuca Indica*) Oil Using Response Surface Technology. Bioresource Technology 2006; 93
498 (3): 379-384.

499 19. Sahoo PK, Das LM, Babu MKG, Naik SN, (2007) Biodiesel Development from High Acid
500 Value Polanga Seed Oil and Performance Evaluation in a CI Engine. *Fuel* 2007; 86 (3): 448-
501 454.

502 20. Mittelbach MP, Remschmidt C, Biodiesel Comprehensive Handbook, Published by M.
503 Mittelbach, Karl-Franzens-Universitat Graz, Graz, Austria. 2004

504 21. Wagner, LE; Clark, SJ and Schrock, MD Effects of Soybean Oil Esters on the Performance,
505 Lubricating Oil and Wear of Diesel Engines. Society of Automotive Engineers. Warrendale, Pa.
506 SAE Paper No. 841 385. 1984

507 22. Schinas P, Karavalakis G, Davaris C, Anastopoulos G, Karonis D, Zannikos F, Stournas
508 S, Lois E, Pumpkin (*Cucurbita Pepo L.*) Seed Oil as an Alternative Feedstock for the
509 Production of Biodiesel in Greece. *Biomass and Bioenergy* 2009;33:44-49.

510 23. Bello. EI, Agge M Performance Evaluation of Egusi Melon (*Citrullus Colocynthis L.*)
511 Seeds Oil Biodiesel. *JETEAS* 2011; 2(5):74-75.

512 24. Willard WP, Engineering Fundamentals of Internal Combustion Engines. Prentice-Hall
513 Limited, Singapore, 1996; 323-325.

514 25. AOCS cd8, 1980.

515 26. Bagby MO, Freedman B, Seed Oils for Diesel Fuels: Source and Properties. SAE Paper
516 No. 87-1583. 1978.

517 27. Knothe G, Dependence of Biodiesel Fuel Properties on the Structure Of Fatty Acid Alkyl
518 Esters, *Fuel Process Technol* 2005;88:1059-1070.

519 28. Laza T, Bereczky C, (2010) Basic Fuel Properties of Rapeseed Oil-Higher Alcohol Blends.
520 *Fuel* 2010;20(2):803-810.

521 29 Goodger EM, Hydrocarbon Fuels. Macmillan Press Ltd., England. 1975

522 30. Joshi, RM, Pegg M Flow Properties of Biodiesel Blends at Low Temperature. *Fuel* 2007; 88
523 (1-2):143-151.

524 31. Alptekin A, Canakci M Characterization of the Key Properties of Methyl Ester-Diesel Fuel
525 Blends. *Fuels* 2009; 88(1):75-80.

526 32. Ladammatos, N and Goacher, J Equation for Predicting the Cetane Number of Diesel Fuels
527 from their Physical Properties. *Fuel* 1995; 74 (7): 1083-1092.

528 33. Schwab AW, Bagby MO, Freedman B, Preparation and Properties of Diesel Fuels from
529 Vegetable Oils. Fuel 1997 66:1372-1378.

530 34. Romano S, Vegetable Oils – A New Alternative. Vegetable Oil Fuels-Proc. Int. Conf. on
531 Plant and Vegetable Oils as Fuels, 106-166, Fargo, N.D. August, St. Joseph. Mich.: ASAE. 1982

532 35. Iyayi AF, Akpata PO, Ukpoyibo U. Rubber Seed Processing for Value-Added Tatex
533 Production in Nigeria. Afri. J. Agri. Res. 2008; 3(7): 505-509.

534 36. Lin, C.Y.; Li, R.J. Fuel Properties of Biodiesel Produced from the Crude Fish Oil from the
535 Soapstock of Marine Fish. Fuel Process. Technol., 2009;90:130–136.

536 37. Satyanarayan M, Muraleedharan C, Methyl Ester Production from Rubber Seed Oil Using
537 Two-step Pretreatment Process. International Journal of Green Energy 2010; 7(1):84-90.

538 38. Oluba OM, Ogunlowo YR, Ojieh GC, Adebisi KE. Physiochemical Properties of and Fatty
539 Acid Composition of Melon Seed Oil. J. Bio. Sci. 2008; 8(4):814-87.

540 39. Alatise VN, Akinhanmi TF. Extraction, Composition Studies and Physiochemical
541 Characteristics of Palm Kernel Oil. Pak. J. Nutri. 2009; 8(6): 800-803.

542 40. Riazi, M.R.; Roomi, Y.A. Use of the refractive index in the estimation of thermophysical
543 properties of hydrocarbons and petroleum mixtures. Ind. Eng. Chem. Res., 2001;(40): 1975–1984.
544

545

546 **Table 1. Properties of Rubber Seed Oil, its Ester and Blends according to ASTM D6751-02 and EN**
547 **14214**

Property	Rubber Seed Oil	B100	B10	B20	ASTM D6751-02	EN 14214
Density kg/m ³ at 25 °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 % (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, 50°C)	4	3	1	2	No.3 max	1
Distillation temperature 90% °C	383	355	-	-	360 max	

549

550

551 **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

552

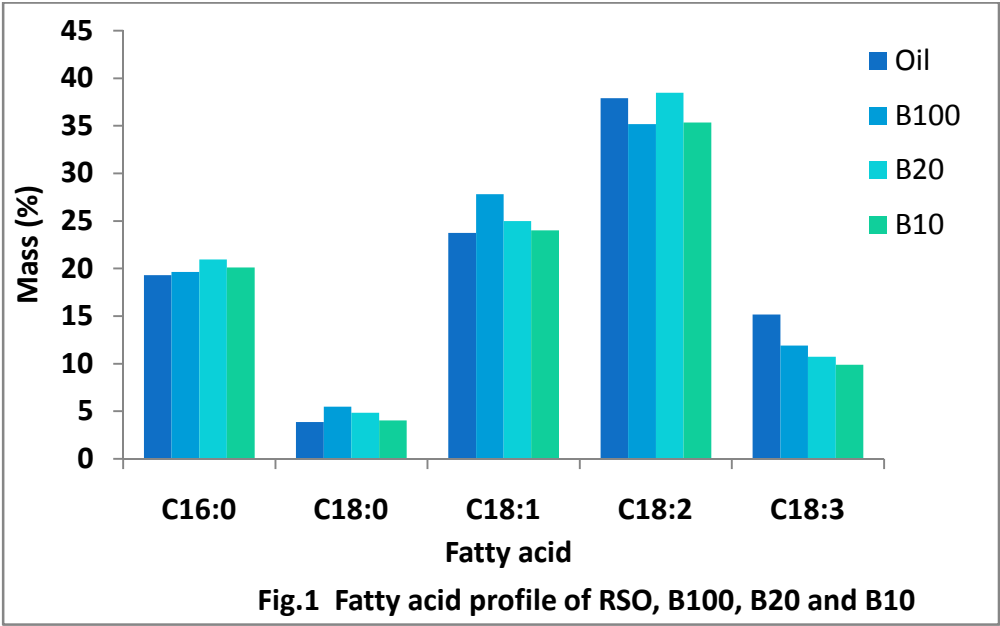
553 **Table 3. Metal components.**

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	0.0029	101.6	4.70	0.35	0.08	0.04		5.0

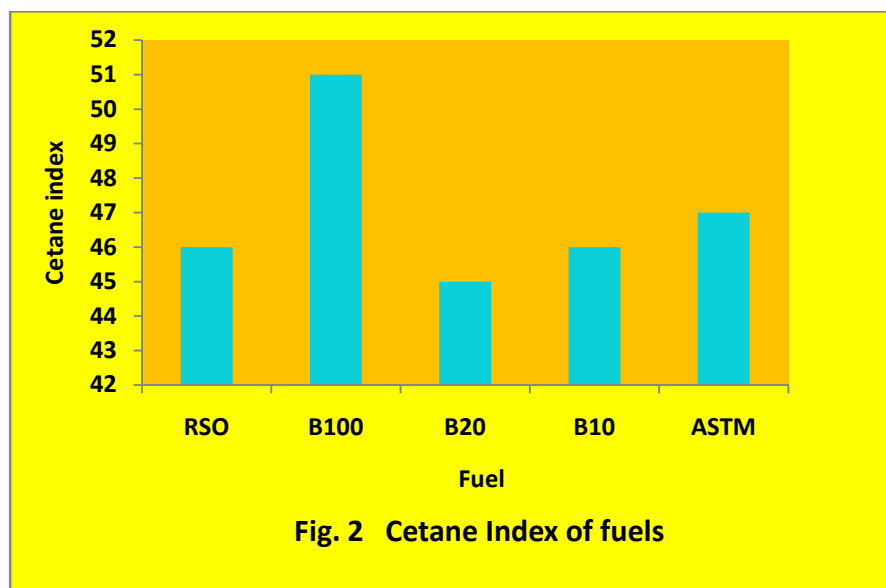
Ca317.933	2							max
Magnesium	0.0009	99.1	1.80	0.60	0.12	0.06		5.0
Mg285.213r	0.20							max
Phosphorous	0.0227	99.1	8.00	2.80	7.00	3.50	0.001	10.0
P212.618r	5							max
Sulphur	0.114	98.7	23.50	6.40	26.90	29.60	0.05	10.0
S180.731r	15						max	max

554

555

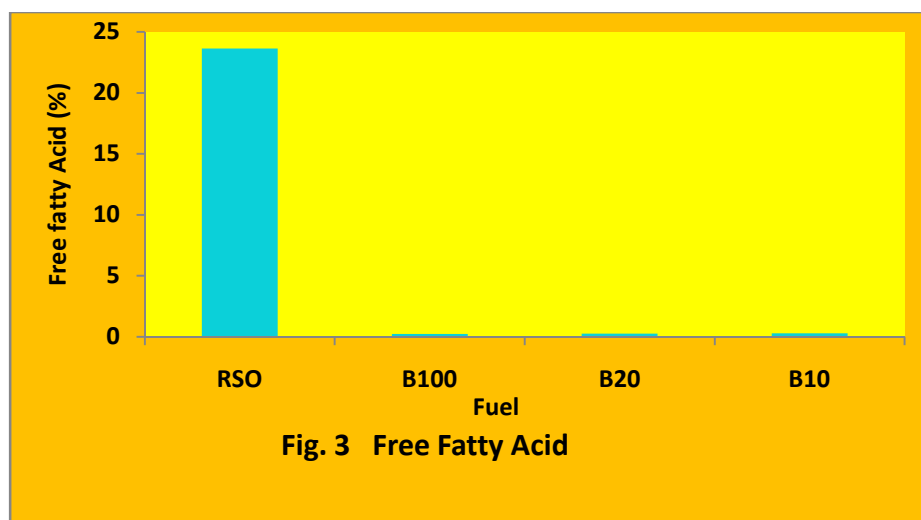


556



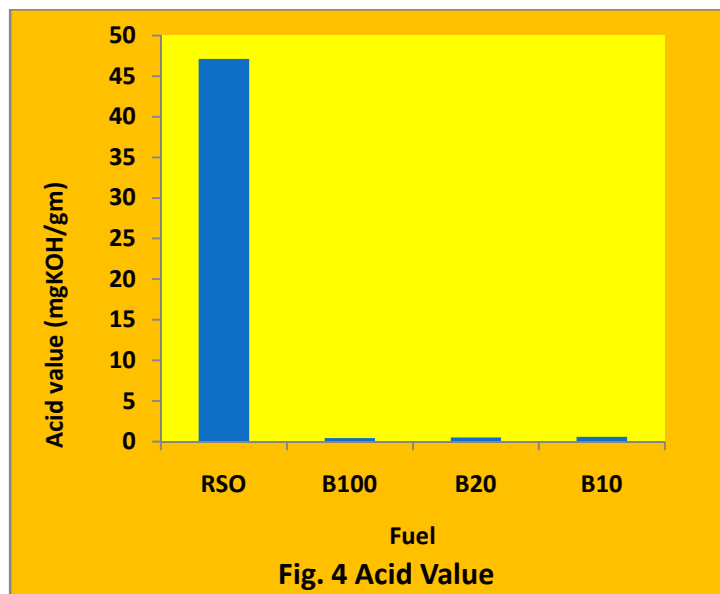
557

558



559

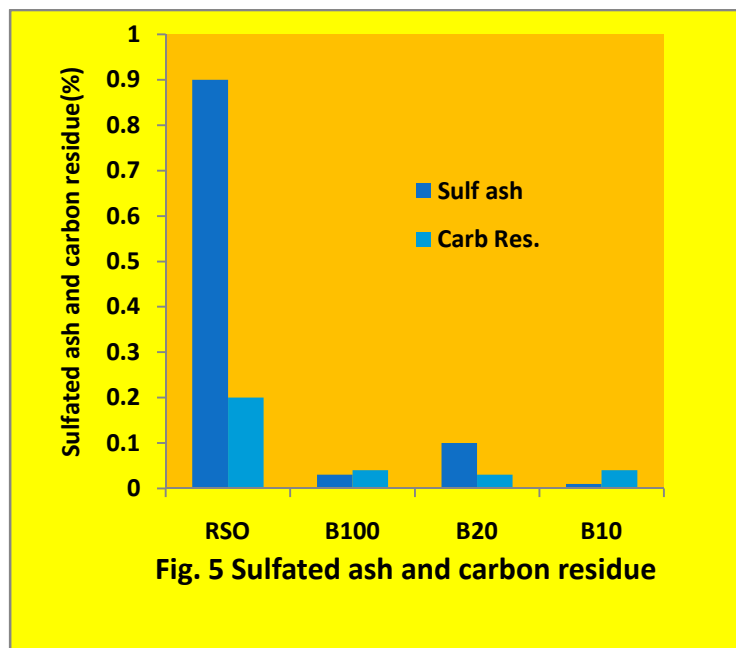
560



561

562

563



564

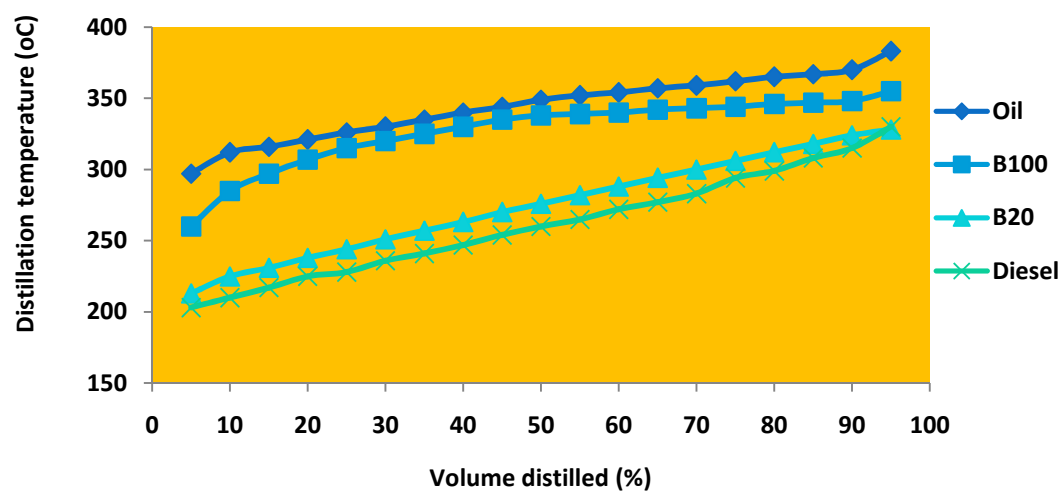


Fig.6 Distillation curves for rubber seed oil, B100 and B20 and diesel