Biological Production of Diesel from Groundnut Seeds

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Abstract: *Environmental pollution, health problems, non-renewability, depletion in supply and hike in price are array of problems linked to continuous reliance on petroleum fossil diesel as energy sources. In order to improve on quality of diesel produced, focus should be shifted to starting material from biological sources. Energy generation from biodiesel is renewable, less toxic, low emission and environmental friendly. This work is aimed at transesterified oil extracted from groundnut seeds into biodiesel. The groundnut seeds were sun-dried for two days and grind into fine particles with grinding machine. The oil was extracted from groundnut seeds by solvent extraction methods. The extracted oil was transesterified to biodiesel using Sulphuric acid as a catalyst. The biodiesel was analyzed by Gas Chromatography Mass Spectroscopic (GC-MS). Physicochemical properties of biodiesel were determined using predictive models based on fatty acid composition and American Society for Testing for Materials (ASTM) protocols. Data obtained were subjected to appropriate statistical analysis. The biodiesel extracted from the groundnut seeds oil had ten fatty acids, namely Palmitic acid: 31.60%, Palmitoleic acid: 5.10%, Stearic acid: 19.30%, Oleic acid: 24.50%, Linoleic acid: 6.90%, Linolenic acid: 6.80, Arachidic acid: 1.3%, Gondoic acid: 1.4%, Behenic acid: 1.5%, Linoceric acid: 1.60%. The highest carbon carbon chain $C_{16} - C_{18}$ of 94.2% was recorded in groundnut seeds diesel while percentage composition of saturated, monounsaturated and polyunsaturated fatty acids in the biodiesel extracted from lipids are 55.30%, 31.00% and 13.70%. The results of physicochemical parameters are Specific gravity: 0.8800; kinematic viscosity: 2.00; flash point: 136; cloud point:-7; pour point:-7; volatile matter: 99.50; refractive index: 1.45; heat of combustion: 36.978; density: 0.8800; Ash content: 0.02; Acid value: 0.3; saponification value: 225; Peroxide: 1.6; iodine values: 45.60; free fatty acids: 1.21; cetane number:75; Oxidative stability: 6.88; long chain saturated factor: 26.00 Cold filter plugging point: 68.22; degree of unsaturation : 65.5; higher heating :42.20 water content: 0.08. Groundnut seeds are ideal and promising alternative starting materials for the production of quality and environmental friendly diesel fuel. The biodiesel produced was in conformity with acceptable standard by regulatory authority.*

Keywords: Groundnut seeds, Solvent lipid extraction, Transesterification, Characterisation, Fossil Diesel

1. INTRODUCTION

The current environmental challenges across the globe have been linked to several human activities in which the use of petroleum fossil fuels is not left out. Ecosystem has suffered a lot as result of various man activities that are detrimental to survival of animals and other living organisms. The problems traced to usage of fossil fuels has affected most developing countries of world and instead of common front towards finding last solution to this menace, there is rapid increase in environmental pollution as a result of persistent usage of conventional fossil fuel.

There have been several activities towards reducing the gasses emanating during the usage of fossil fuels but effort was to no avail as there is increase in discharge and release of those gasses to the environment. Apart from environmental pollution that has resulted in various respiratory and internal health problems, the cost of conventional fuel is not affordable and supply will soon depleted. Despite increase in problems linked to fossil energy source, there is still growing interest in search for more petroleum fuels by governments around the world, this can be liken to overreliance on proceed from petroleum for economic and infrastructural development among developed country in the world.

As a result of declining in the fossil fuels sources and increase in its cost, there is current effort towards find alternative source of energy. The alarming rate of depletion of non-renewable source of this fuel is also one of the contributing factors that awake concern authority towards this new development. Recently, Biofuels have become more attractive alternative fuel because of its renewability, less toxic and positive environmental benefits. It burns up to 75% cleaner than fossil fuels. It substantially reduces unburned hydrocarbons, carbon monoxide and particulate matter in exhaust fumes which cause cancer. Also, it is a much better lubricant than fossil fuels and extends engine life [1, 2].

Biofuels increase safety in storage and transport because they are non-toxic and biodegradable [3]. Biofuels have been described as safe fuels, because the flash point is more than 100°C higher than that of diesel and was given as 160°C which showed that it can be classified as a non-flammable liquid; the toxicity is at least 15 times less than diesel [4]. The oxidation stability of biodiesel fuels was found to be lower and hygroscopic. As solvents they cause corrosion of component, attacking some plastic materials used for seals, hoses, paints and coatings. They showed increased dilution and polymerization of engine sump oil, thus requiring more frequent oil changes.

Also, it is noteworthy that Krawczyk [5] identified biodiesel as a possible replacement to fossil's fuels as the world's primary energy source. Biodiesel could be obtained from an array of agricultural produce such as soybean, groundnut etc. One of the vegetable oils suitable for biodiesel production is ground nut (*A. hypogaea*) oil that is widely cultivated in northern Nigeria. It is a leguminous crop that is cultivated mostly in the sub tropic and tropic regions of the world. The pods are attached to the roots and are very rich in oil, which is extracted by roasting, grinding and pressing. The oil is commonly used as cooking oil because of its high protein content.

Groundnut oil has been reported to be among the most consumed vegetable oil and the 13th most important food crop in the world. It is also known to contain a high percentage of unsaturated fatty acid namely oleic and linoleic acid and low free fatty acid value. Groundnut seed contain high quality edible oils, protein, and carbohydrate. Globally, 50% of groundnut produced is used for oil extraction, 37% for confectionary use and 12% for seed purpose. The fat in the oil is approximately 50% monounsaturated, and 30% polyunsaturated. In comparison, groundnut oil has been reported of having capacity to produce approximately 123 gallons of biodiesel per acre while soybeans yield only 50 gallons.

Nigeria is the third largest producer of groundnut after China and India (SATRENDS, 2001). In 1994, 1,453,000 tons of groundnuts were produced in the country. While in 1998, 2,227,000 tons of the crops were produced in the country [6]. The Nigerian oil mill company in Kano, Kano State, Nigeria crushes between 100–120 tons of groundnut seeds a day during their oil production season [7]. In addition, there are numerous oil mills (both large-scale and low-scale industries) which ensure the production of groundnut oil throughout the year. Therefore, the availability and abundance of the oil makes it a candidate for being used for the production of biodiesel in Nigeria.

Despite the fact that Nigeria is third largest production of groundnuts, limited or no work has been reported on the production of groundnut biodiesel as a fuel for diesel engine. This work is focus on production and characterization of diesel obtained from groundnut seeds. The objectives of this work includes, Extraction of oil from groundnut seeds, trans-esterification of groundnut oil to Fatty Acid Methyl Ester and characterization of the ethyl esters produced from groundnut oil.

2. MATERIALS AND METHODS

2.1 Sample collection

The groundnut seeds were purchased from market at Esa-oke, Osun state, Nigeria. The groundnut seeds were taken to the Biology laboratory at department of Science Laboratory; Osun State College of Technology, Esa Oke, Osun State. The groundnut seeds were sun-dried for seven days and finally grounded into fine powdery form with aid of electronic blender.

2.2 Extraction of oil from Groundnut seeds

This was carried out by the Bligh and Dyer method [8] modified by Nascimento *et al.*, [9]. A mixture of 2 ml methanol and 1 ml chloroform (2:1) was made and added to 1g grinded groundnut seeds. The mixture was kept for 24 h at room temperature to dissolve the lipids/oils properly. It was centrifuged at 3000 rpm for 10 min and supernatant was collected. The process was repeated by adding 2 mL of chloroform to the pellet and shaken properly. It was again centrifuged at 3000 rpm for 5min and supernatant was separated. After adding 2 mL of 1% potassium chloride (KCL) to the supernatant, two separate layers were formed. The upper layer (methanol/powdered groundnut seeds) was decanted and the lower chloroform layer containing the extracted lipids was collected in another test tube. The upper layer (methanol/powdered groundnut seeds) was extracted again using the same procedure but with 1 mL of 1% potassium chloride (KCL). The bottom phase (chloroform/lipids) were combined and evaporated for 24 h in a drying oven at 80°C.

2.3 Trans-esterification of Groundnut oil to Fatty Methyl Ester (FAME)

This was achieved using the Lepage and Roy [10] method, with slight modifications by Anitha and Sriman [11]. The crude oils (about 10 mg) was dissolved using 2 mL of a freshly prepared mixture of chloroform-methanol (2:1, v/v) in a 10 mL Pyrex tube with a Teflon-sealed screw cap. 1 mL of methanol as reagent and 0.3 mL of sulfuric acid 95-97 % (Scharlau Chemie, reagent grade) as catalyst was added, for the trans-esterification of about 10 mg of lipids. After screwing the lid, the tube with the mixture was weighed and vigorously shaken for 5 min. Finally, the tube was incubated at 100 °C for 10 min and cooled to room temperature. Followed by addition of 1 mL of distilled water for phase separation (by adding water two distinct phases are formed, the upper layer rich in water, methanol, glycerol, and sulphuric acid, and the lower layer rich in chloroform and esters). Then, 1 mL of distilled water was added for a gentle water washing of esters with chloroform layer (more dense than the water layer) followed by discard of the water rich upper layer (less dense). This step was repeated twice more. The esters rich layer was filtered using a disposable Nylon syringe filter (0.2 μm pore, 13 mm diameter, Cronus, UK). The chloroform was then evaporated to dryness from the esters in a laboratorial hood, at room temperature (of about 25 °C).

2.4 Gas Chromatography and Mass spectroscopic of Groundnut Fatty Acid Methyl Ester

The FAME obtained from the groundnut oil was analyzed according to the method described by Medina *et al.* [12] using a Shimadzu 2010 gas chromatography (Shimadzu Scientific Instruments, Columbia, MD, USA) equipped with a flame Ionization detector and a diethylene glycol succinate capillary column ($30m \times 0.25 \times 0.25$ μm). Both initial column temperature and injection port temperature were $180^{o}C$. Detector temperature is $230^{o}C$, and was increased to $300^{o}C$ at a temperature gradient of $15^{o}C/min$. Biodiesel sample (100 μL) was placed into capped test-tubes, saponified with 1 ml of saturated $KOH-CH_3OH$ solution at $75^{o}C$ for 10min, and then it was subjected to methanolysis [13] with 5% HCL in methanol at $75^{o}C$ for another 10 min. Thereafter, the Phase containing the fatty acid methyl esters was separated by adding 2 mL of distilled water, and methanol was recovered. The components were identified by comparing their retention times and fragmentation patterns with those of the standards. Six fatty acid methyl esters (C16:1, C17:0, C18:1, C18:2 and C18:3) were used as the standard materials.

2.5 Physicochemical Characterization of the Coconut Methyl Esters Produced

2.5.1 Specific Gravity

A 3ml aliquot of the methyl ester was weighed and its density calculated using the equation below

$$\text{Density (\%)} = \frac{\text{Mass of Methyl ester(g)}}{\text{Volume of water(ml))}} \text{ x100}$$

Then, the specific gravity of the methyl ester was calculated using the formula in equation below

$$\text{Specific gravity (\%)} = \frac{\text{Density of Methyl Ester (g)}}{\text{Density of water(g)}} \text{ x100}$$

2.5.2 Relative density

This was carried out using the method described by ASTM D6751 [14]. The mass was obtained by weighing the empty and filled (Groundnuts methyl ester) Erlenmeyer flask. The difference was the mass of the groundnuts methyl ester. With these two values, the density was obtained, which is mass divided by volume.

2.5.3 Moisture content

This was determined by method described by AOCS. Cd 3-25 [15] An empty flask was weighed with and without the amount of methyl ester and dried in an oven at $105^{o}C$ for 7h, weighing each 2 hours till a constant weight was obtained, and finally the weight was taken and compared with the initial recorded weight. The percentage moisture content was calculated using below following equation.

$$\text{Moisture content (\%)} = \frac{(W1-W2)\ (g)}{W2(g)} \text{ x100}$$

Where,

W_1 = Original weight of the sample before drying

W_2 = Weight of the sample after drying

2.5.4 Viscosity

This was done using the method of AOAC [16]. The methyl ester was gradually poured into the viscometer until its lobe was almost filled and then it was placed in a water bath and allowed to heat up to an equilibrium temperature of 40^oC. The methyl ester on the broad arm was sucked through the narrow arm until it reached the upper mark above the lower lobe of this narrow arm. The methyl ester was then allowed to flow back to the lower mark just below the lower lobe. The time taken for the flow (flow time, t) was recorded. Then, the viscosity was calculated using below equation:

$$\text{Viscosity (\%)} = \frac{Vp1t1}{p2t2} \times 100$$

Where,

n = Viscosity of the methyl ester mm^2/s

v = Viscosity of water mm^2/s

p_1 = Density of the methyl ester, Kg/m^3

p_2 = Density of water, Kg/m^3

t_1 = Time taken for the groundnuts methyl ester to flow back

t_2 = Time taken for the water to flow back

2.5.5 Flash Point

The flash point was determined according to open cup method described by ASTM D6751, [14]. The cup was filled with a sample of the methyl ester up to the mark (75ml) and the cup was heated with a bunsen burner maintaining a small open flame from an external supply of natural gas. Periodically, the flame was passed over the surface of the methyl ester. When the flash temperature was reached the surface of the methyl ester caught fire. The temperature (at the moment) was noted and recorded as the flash point temperature.

2.5.6 Cloud Point

This was carried out based on the ASTM D6751, [14] method. A test tube with a thermometer inserted in it, was filled with a sample of the methyl ester. The methyl ester was cooled at 2^oC/min rate and continuously monitored until a white cloud appeared on the bulb of thermometer. The temperature that corresponds to the first formation of a cloud in the methyl ester was recorded.

2.5.7 Pour Point

This was carried out using method described by ASTM D 97-96a [17]. A sample of the methyl ester in a capillary tube was solidified; thereafter, it was attached to a thermometer and inserted into a gradually heating beaker of water. The temperature at which the sample started moving in the capillary tube was recorded as pour point.

2.5.8 Percentage ash content

The ASTM D874, [18] method was used for the determination of percentage ash content. To a washed porcelain crucible, One gram of groundnuts methyl ester was added. It was weighed after drying and cooling in an oven at 100^oC and a desiccator respectively. Then, heated for 4 hours at 600^oC inside a muffle furnace, after which it was removed and subsequently cooled in a dessicator and weighed again. The percentage ash content was calculated using below equation:

Ash content (%) $= \frac{A-B}{C}$ x100

Where,

A = Weight of crucible + ash,

B = Weight of crucible

C = Weight of original sample

2.5.9 Refractive Index

This was determined according to the method of Alamu *et al*. [19] using a refractometer (Abbe refractometer bench). The power switch was turned on; the illuminating lamp came up and the display showed 0000. A drop of the methyl ester was introduced on the working surface of the lower refracting prism. The rotating arm and the collecting lens cone of the light gathering illuminating units were rotated so as to make the light-intake surface of the upper light-intake prism to be illuminated evenly. The field of view was observed through the eye piece and the adjustable hand wheel was rotated so as to make the line dividing the dark and light areas fall in the cross line. The dispersion correction hand wheel was rotated so as to get a good contrast between the light and dark area and minimum dispersion. The read button was pressed and the refractive index was displayed on the screen

2.5.10 Conductivity

This was determined using a conductivity meter. The conductivity meter was standardized with 0.01M KCl solution. The electrode was rinsed with deionized water, wiped and dipped into a sample of the ethyl ester and left for some time to stabilize the reading. The reading was displayed on the screen and then recorded in micro Siemens per centimeter (μS/cm).

2.5.11 Heat of Combustion

This was carried out using a bomb calorimeter by method of AOAC [16]. The calorimeter was standardized using benzoic acid. To a crucible of the calorimeter, a weighed amount of the methyl ester (1.058g) was added and the fuse wire was attached between the electrodes. Thereafter, it was placed in the bomb, which was pressurized to 18atm of oxygen. The bomb was placed in a vessel containing a measured quantity of water (2000g). The ignition circuit was connected and the water temperature was noted. After ignition, the temperature rise was monitored every minute till a constant temperature was reached and recorded. The pressure was released, the length of unburned fuse wire was measured and the residue titrated with 0.7M of sodium carbonate solution using phenolphthalein as indicator. The heat of combustion was calculated using below equation:

Heat of Combustion $= \frac{E\Delta T - 2.3V}{g(KJ/Kg)}$ x100

Where,

 E = Energy equivalent of the calorimeter using benzoic acid

ΔT = Temperature rise

L = Length of burnt wire

V = Titration volume

g = Weight of sample

2.5.12 Acid Value

This was determined by method of ASTM D6751 [14]. A standard alcoholic KOH solution (0.5M) was prepared by dissolving KOH (pellet) with ethanol. The solution was then filtered and stored in brown bottle for Five days. Furthermore, a mixture of 95% ethanol and diethyl ether in a ratio of 1:1 (v/v) was prepared. 5 grams of the methyl ester was dissolved in 25ml of 1:1 (v/v)

mixture of ethanol and diethyl ether. The solution was titrated with 0.5M ethanolic KOH solution in the presence of 5 drops of phenolphthalein as indicator until the end point (colorless to pink) was recognized. The total acidity (acid number) in KOH/g was calculated using below equation.

$$\text{Acid value} = \frac{V \times N \times 56.1}{M}$$

Where,

V= Volume expressed in milliter of 0.5M solution of ethanolic KOH,

M= Weight of the sample in gram

N= Concentration of ethanolic KOH

2.5.13 Peroxide Value

The method of AOAC [16] was used for the determination of peroxide value. To a 30 ml of mixture of glacial acetic acid and chloroform (3:2, v/v), 2.206g of the methyl ester was dissolved in the mixture, then, 20% of potassium iodide (0.5 ml) was added and the solution swirled in the dark for one minute after which 75ml of distilled water was added. The mixture was titrated with 0.1M sodium thiosulphate with vigorous shaking until the yellow colour of the iodine had disappeared. Starch indicator (0.5ml) was added then to obtain a blue colour and titration continued until all the blue colour had disappeared. The peroxide value was calculated using below equation:

$$\text{Peroxide Value} = \frac{(S-B) \times M \times 100}{\text{Sample weight(g)}}$$

Where,

S = Sample titre value in ml

B = Blank titre in m

M = Molarity of Sodium thiosulphate

2.5.14 Iodine Value

This was determined using the method of AOAC [16]. An aliquot of the methyl ester (0.8825g) was weighed into a conical flask, tetrachloromethane (15ml) and 25 ml of Wig's solution was added. This mixture was placed in a stoppered conical flask, swirled gently and placed in a dark cupboard for one hour after which 20 ml of 20% potassium iodide solution and 100ml of distilled water were added. After gentle shaking, liberated iodine was titrated with 0.1M sodium thiosulphate solution until the yellow colour of the iodine had appeared. Starch indicator (1ml) was added then to obtain a blue colour and titration continued until all the blue colour had disappeared. The iodine value was calculated using below equation

$$\text{Iodine Value} = \frac{(B-S) \times M \times 100}{\text{Sample weight(g)}}$$

Where,

S = Sample titre value in ml

B = Blank titre in ml

M = Molarity of Sodium thiosulphate

2.5.15 Percentage Free Fatty Acid

This was carried out using the method of AOAC [16]. Two grams of the methyl ester was weighed into a conical flask and 10 ml of 95% ethanol was added. This was then titrated with 0.1 M sodium hydroxide using phenolphthalein as an indicator. The conical flask was shaken constantly until a pink colour that persisted for 30 seconds was obtained. The percentage free fatty acid was obtained from the equation below

$$\text{Free Fatty Acid} = \frac{V \times M \times 2.92}{\text{Sample weight(g)}} \times 100$$

Where,

V= Volume of 0.1M Sodium hydroxide used in ml

M= Molarity of NaOH.

2.5.16 Determination of other Properties Based on Fatty Acid Methyl Esther (FAME) Profiles

This was achieved using predictive models of Fatty Acid composition. Saponification value (SV), iodine value (IV), Cetane number (CN) degree of unsaturation (DU), long chain saturated factor (LCSF) and cold filter plugging point (CFPP) was determined by equations proposed by Islam *et al* . [20]:

$SV = \sum (560 \times A_i) / M_{wi}$

$IV = \sum (254 \times A_i \times D) / M_{wi}$

$CN = 46.3 + (5458/SV) – (0.225 \times IV)$

$DU = \sum MUFA + (2 \times PUFA)$

$LCSF = 0.1 \times (C16:0, wt\%) + 0.5 \times (C18:0, wt \%) + 1 \times (C20:0, wt \%) + 1.5 \times (C22:0, wt\%) + 2.0 \times (C24:0, wt\%)$

$CFPP = (3.1417 \times LCSF) – 16.477$

Where, D is the number of double bonds, M_W is the fatty acid (FA) molecular mass, and A_i is the percentage of each fatty acid (FA) component of the microalgae oil.

The kinematic viscosity (υ), density (*ρ)* and higher heating value (HHV) of each Fatty Acid Methyl Ester (FAME) were determined by equation proposed by Ramirez-Verduzco *et al*. [21]:

$In (v_i) = -12.503 + 2.496 + In (M_i) -0.178 \times N$

$\rho = 0.8463 + 4.9/M_i + 0.0118 \times N$

$HHV_i = 46.19 – 1794/M_i – 0.21 \times N$

Where,

(*vi* is the kinematic viscosity of at 40 °C in mm2/s; *ρi* is the density at 20 °C in g/cm3; *HHVi* is the higher heating value in MJ/kg of *i*th FAME, N is the number of double bonds, M_i is the molecular mass of each fatty acid component.

Predictive oxidative stability was calculated based on C18:2 and C18:3 content of Fatty Acid composition as suggested by Park *et al*. [22]:

$OS= 117.9295/ (wt\% C_{18.2} + wt\% C_{18.3} + 2.5905 (0<100)$

Where,

wt% $C_{18.2}$ is the content of linoleic, wt% $C_{18.3}$ is the content linolenic acids (wt%) $(0 < X < 100)$; and *OS* is the oxidation stability in hours.

3. RESULTS AND DISCUSSION

The composition, quality and quantity of fatty acids in biodiesel of groundnut oil were examined through gas Chromatography and Mass spectroscopy analysis. The biodiesel extracted in the groundnut oil had ten fatty acids, namely Palmitic acid: 31.60%, Palmitoleic acid: 5.10%, Stearic acid: 19.30%, Oleic acid: 24.50%, Linoleic acid: 6.90%, Linolenic acid: 6.80%, Arachidic acid: 1.3%, Gondoic acid: 1.4%, Behenic acid: 1.5% and Linoceric acid: 1.6% (Table 1). The highest carbon Carbon chain $C_{16} - C_{18}$ of 94.2% was recorded in *groundnut diesel* while percentage composition of saturated, monounsaturated and polyunsaturated fatty acids in the biodiesel extracted from oil were 55.30%, 31.00% and 13.70% respectively (Table 1).

Table 1: Gas chromatography and mass spectroscopy of Groundnut oil diesel showing fatty acids composition in percentage of total fatty acid methyl esters components

Fatty Acids	Molecular Formular	*Groundnut diesel*
		Percentage Composition of each Fatty Acids
Palmitic Acid	$C_{16}H_{32}O_2$	31.60
Palmitoleic Acid	$C_{16}H_{30}O_2$	5.10
Stearic Acid	$C_{18}H_{36}O_2$	19.30
Oleic Acid	$C_{18}H_{34}O_2$	24.50
Linoleic Acid	$C_{18}H_{32}O_2$	6.90
Linolenic Acid	$C_{18}H_{30}O_2$	6.80
Arachidic Acid	$C_{20}H_{40}O_2$	1.3
Gondoic Acid	$C_{20}H_{38}O_2$	1.4
Behenic Acid	$C_{22}H_{44}O_2$	1.5
Linoceric Acid	$C_{24}H_{48}O_2$	1.60

$C_{16} - C_{18}$ (%)	94.2
Saturated Fatty Acid (%)	55.30
Monounsaturated Fatty Acid (%)	31.00
Polyunsaturated Fatty Acid (%)	13.70

The specific gravity of the groundnut ethyl ester obtained in this study is 0.88 (Table 2). The specific gravity obtained was found to be within the limits of EN 14214 (0.86 – 0.90) biodiesel fuel standard. This is similar to work of Alamu *et al*. [19] that reported specific gravities of 0.883 and 0.876 for both palm kernel oil ethyl esters and (0.883) rapeseed oil ethyl esters.

The value recorded for viscosity of the groundnut oil ethyl esters at 40 °C in this work is 2.00 mm^2/s (Table 2); this value is within the limits of ASTM D6751 (1.9 – 6.0 mm^2/s) biodiesel fuel standard.

The flash point of the groundnut methyl ester recorded in the present study is 136°C (Table 2). The value was also found to be above the minimum value (120 °C) of the EN 14214 and (130°C) of the ASTM D6751 biodiesel fuel standard. In contrary to the above study, Alamu *et al*. [19] reported 167°C, 177°C, 178°C and 182°C flash points for palm kernel oil biodiesel, Canola ethyl esters, sunflower ethyl esters and olive ethyl ester. The value of flash point observed in this study for groundnut oil biodiesel showed the presence of little or no residual alcohol and is of prime importance for prevention of fire outbreak in the compressor engine when used as fuel, also important for storage and transportation of the fuel [23].

The cloud point value for the groundnut biodiesel in this work is -7°C (Table 2). The value is within the required limits of ASTM D6751 (-3 to 12°C) for biodiesel fuel. This was in line with work of Alamu *et al*. [19], which reported that the cloud points of -6

and -10°C for canola and rapeseed ethyl esters respectively. The lower cloud point recorded in this work showed that the biodiesel produced is good as fuel in regions where temperature is between 5 and -10°C.

The pour point recorded in this study the groundnut oil ethyl ester is -7°C. . The pour point of the groundnut oil ethyl ester is found to be within the regulatory standard of ASTM D 6751 (-15 to 10°C) for biodiesel. In related to the above work, Anastopoulos et al. [29] reported -6, -8 and -5°C pour point values for sunflower ethyl esters, rapeseed ethyl esters and olive ethyl esters. The lowered pour point implies that the groundnut oil ethyl ester can be used as fuel in regions where the temperature is within the range of -5 to -10°C.

The volatile matter for the groundnut biodiesel is 99.50 (Table 2). The value of volatile matter in this study conforms satisfactorily with required biodiesel standard (US (ASTM D6751- 08).

The refractive index of groundnut methyl ester in this study is 1.45 (Table 2). In related view, Deshpande and Kulkarni [25] reported refractive index of 1.430 and 1.431 for palm oil and ghee biodiesel. The above work is also similar to work of Ibeto et al. [26] that reported 1.463 for refractive index of groundnut oil biodiesel.

In the present study, the heat of combustion of the groundnut biodiesel is 36.978 MJ/kg (Table 2). In related vein, Anastopoulos et al., [24] reported 38.6 MJ/kg and 39.2 MJ/kg heat combustions for sunflower and olive biodiesel while Lang et al. [27] reported heat combustions of 40.97 and 39.65 MJ/kg for rapeseed oil and linseed oil biodiesel.

Conductivity is a measure of the ability of water to pass an electrical current, it is indicative of the presence of water in the biodiesel [28]. The conductivity of the groundnut ethyl ester in the current study is 0.00μS/cm (Table 2). This could be due to proper drying and short storage time before the test was carried out.

The density of groundnut biodiesel is 0.8800 and it fall within the standard range (0.86 – 0.90g/cm^{3}) (Table 2).

The ash content is a measure of the amount of residue left when the fuel is heated to 600°C [28]; the value observe for groundnut biodiesel in this work is 0.02% (Table 2). The ash content of the groundnut oil ethyl ester was found to be above the limit of ASTM D 6751 (0.01%), but was within the required limit of EN 14214 (0.02%) for biodiesel fuel. This is in line with work of Rashid et al. (2010) that reported 0.016% for ash content of Jatropha biodiesel.

The acid value of the groundnut biodiesel (0.3) in this study is within the required limits of the ASTM D6751 (0.5mgKOH/g maximum) and EN 14214 (0.5mgKOH/g maximum) for biodiesel standards (Table 2). This is similar to the work of Lang et al. (27) that reported 0.265 and 0.324mgKOH/g acid values for canola oil and linseed biodiesels. In dissimilar view, Kumar et al. [29] reported acid value of 0.18 for groundnut oil biodiesel. The low acid value of the groundnut oil ethyl ester indicates that the fuel contains relatively little or no water which could hydrolyze the biodiesel to free fatty acids.

In this study, the value reported for biodiesel saponification is 225 (Table 2). This is contrary to findings of Anastopoulos et al. [24] that reported saponification values of 192.1, 170.4, 196.2 and 193.2mgKOH/g for sunflower oil ethyl ester, rapeseed oil ethyl ester, olive oil ethyl ester and used frying oil ethyl ester respectively.

The peroxide value of the groundnut oil ethyl ester is 1.60meq/Kg (Table 2). The low peroxide value of the groundnut biodiesel could be as a result of low level of unsaturated fatty acids (as indicated by the iodine value of the ethyl ester). Also, proper storage and handling of the groundnut oil ethyl ester to avoid contaminants and factors that enhance autoxidation could have contributed to the low peroxide value.

The iodine value of the groundnut biodiesel is 45.60mgI^{2}/g (Table 2). The iodine value of the groundnut biodiesel is within the limits of EN 14214(120 mgI^{2}/g maximum) biodiesel fuel standard. This implies lower degree of unsaturation and better oxidative stability of the groundnut biodiesel.

The value recorded for free fatty acids (%) in this study for groundnut diesel is 1.21 (Table 2).

Cetane number is one of the primary indicators of a good diesel fuel quality and is related to the ignition delay time a fuel experiences once injected into a diesel engine combustion chamber [30]. The groundnut oil biodiesel had empirically calculated cetane number of 72 (Table 2) which is above the minimum value of the ASTM D6751 (40 minimum) and EN 14214 (51 minimum) international biodiesel fuel standards. In dissimilar to the above work, Reddy and Ramesh [31] and Owolabi et al., [32]

reported cetane number of 55 and 51 for Jatropha biodiesel, waste cooking oil biodiesel and coconut biodiesel respectively. Thus, the higher cetane number of groundnut biodiesel in this study shows a shorter ignition delay time.

Oxidative stability (hours) of 6.88 observed in biodiesel obtained from groundnuts conforms satisfactorily to ASTM D6751- 08 and EN 14214 biodiesel standard (Table 2).

The biodiesel obtained from oil extracted from groundnut had 26.00 long chain saturated factor (LCSF) while 68.22 was recorded in biodiesel of groundnut for Cold filter plugging point. The degree of unsaturation in groundnut biodiesel is 65.5, the higher heating value 42.20 while water content is 0.08 (Table 2).

Table 2: Physico-chemical properties of the biodiesel obtained from groundnut seeds in comparism with US (ASTM) D6751-08 and Europe (EN 14214) standard

S/N	Physicochemical parameters	*Groundnut seeds*	USA (ASTM) D6751-08	EUROPE (EN 14214)
1	Specific Gravity	0.8800	0.88	
2	Kinematic Viscosity (mm^2/s) at 40^{0}c	2.00	1.9-6.0	3.5-5.0
3	Flash Point (^{0}C)	136	130min	120min
4	Cloud Point (^{0}C)	-7	-3-+12	-
5	Pour Point (^{0}C)	-7	- 15 - +10	-
6	Volatile Matter (%)	99.50		
7	Refractive Index	1.45	1.479	
8	Heat of Combustion (MS/kg)	36.978	35min	35min
9	Conductivity (MS/cm)	0.00		
10	Density (g/cm^3)	0.8800	0.86-0.90	
11	Ash Content (%)	0.02	0.01	0.02
12	Acid Value (mgKOH/g)	0.3	0.5	0.5
13	Saponification Value (mgKOH/g)	225		
14	Peroxide Value (meq/kg)	1.6		
15	Iodine Value (mgI$_2$/g)	45.60		120max
16	Free Fatty Acid (%)	1.21		
17	Cetane Number	75	47min	51min
18	Oxidative Stability (hr)	6.88		3.0min
19	Long Chain Saturated Factor (LCSF)^{0}C	26.00		
20	Cold-Filter Plugging Point (CFPP)	68.22		
21	Moisture Content (%)			
22	Degree of Unsaturation	65.5		
23	High Heating Value (HHV)	42.20		
24	Water Content	0.08	500ppm	500max
25	Calorific Value (Kcal/kg)			

4. CONCLUSION

Groundnuts seeds can be converted to methyl esters through solvent extraction of oil from grinded groundnuts seeds and trans esterification. The properties of the biodiesel obtained are within the regulatory standard set by USA (ASTM 06751-08) and EUROPE (EN 14214). The pour point is $-7^{o}C$ which means it cannot be used when temperature can fall below this value. Findings from this study show that the diesel obtained from groundnuts seeds is a perfect alternative to fossil diesel. In view of the similarity of the properties to those of diesel fuel, it can hence be used as replacement fuel for diesel engines.

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