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# PRODUCTION AND CHARACTERIZATION OF BIODIESEL FROM PALM OIL SLUDGE AND PALM KERNEL OIL USING NON-HEATING METHOD

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## ABSTRACT

Biodiesel was produced from palm oil sludge (POS) and palm kernel oil (PKO) by agitation at room temperature. Physicochemical properties of the POS and PKO were determined. Properties measured for POS, white PKO and the black PKO respectively were acid value (78.877, 8.799 and 7.106 mg KOH/g), free fatty acids (39.44, 4.39 and 3.55%), saponification value (212.60, 253.29 and 258.96 mg/g), iodine value (32.74, 13.33 and 36.32 g/g), specific gravity (0.884, 0.881 and 0.884 g/cm$^3$), peroxide value (0.70, 1.00 and 1.40 meq $O_2$/kg). They all met the specifications for biodiesel production. Biodiesel produced yielded percentage conversion of 89%, 86% and 87% for POS, white and the black PKO methyl esters respectively. Biodiesel quality parameters: specific gravity (0.871 g/cm$^3$), kinematic viscosity (3.21-4.90 mm$^2$/s), cetane number (48-49), flash point (85-111 ºC), acid value (0.44-1.12 mg KOH/g), sulphur content (0.0197-0.0378%), ash content (0.00-0.01%), moisture content (0.01%), cloud point (5-13 ºC) and pour point (-9.0-10.0 ºC) were within the stipulated ASTM limits. Flash point of the black palm kernel oil methyl esters (BPKOME) was below the minimum limit (100-170 ºC). The GCMS of the fatty acid methyl esters showed fatty acid profiles rich in palmitic, and oleic acids indicating that these FAMEs can serve as fossil diesel substitute.

**Keywords:** Biodiesel, Esterification, Fossils, Oil, Quality

## INTRODUCTION

Diesel fuel is one of the products created from crude oil. Petroleum diesel, also called petro diesel, or fossil diesel is the most common type of diesel fuel. It is produced from fractional distillation of crude oil between 200 ºC (392 ºF) and 350 ºC (662 ºF) at atmospheric pressure, resulting in a mixture of carbon chains that typically contain between 8 and 21 carbon atoms per molecule [1].

Supply of fossil fuels, nonrenewable energy source, is threatening to run out in a foreseeable future as reports have it that many of the oil fields are experiencing decline in oil reserve [2, 3]. Biodiesel is an alternative fuel for diesel engines similar to conventional or fossil diesel that can be produced from straight vegetable oils, animal fat/oils, tallow and waste cooking oil. Biodiesel can be produced from any material that contains fatty acids, be they linked to other molecules or present as free fatty acids. Thus various vegetable fats and oils, animal fats, waste greases, and edible oil processing wastes can be used as feedstock for biodiesel production. The choice of feedstock is based on such variables as local availability, cost, government support and performance as a fuel [4].

Biodiesel offers many advantages such as: it is renewable, energy efficient, nontoxic, sulphur free and biodegradable, and also it usually takes cleaner combustion and reduces global warming gas emissions from the diesel engines. Specifically, the combustion of vegetable oil biodiesel does not add to the net $CO_2$ in the atmosphere, because the next crop will reuse $CO_2$ to grow [5, 6]. The major drawback to the sustainability of the commercialization of biodiesel as a viable replacement for diesel (petroleum) includes limited quantity of non-edible feedstock, hence, the need to source for a feedstock that is both non-edible and available in abundance.

Nigeria, as one of the world's major producers and exporters of palm oil, ranked as the 5$^{th}$ largest producers of palm oil in the world [7], is also producing large amount of low-grade oil such as Palm Oil Sludge and Palm Kernel Oil. The use of PKO can lower the cost of biodiesel production significantly, which make them highly potential alternative feed stocks for biodiesel production. According to Graboski *et al.* [8] the fatty acids compositions of oils have strong influence on the properties of biodiesel. These properties are both physical and chemical properties, including the fuel properties (flash point, cetane number, viscosity, density and pour/cloud point among others).

Lots of researches have been done and are still ongoing on biodiesel production. However, this research seeks to investigate the properties of the biodiesel produced from palm oil sludge and palm kernel oil. The study was carried out to produce and characterize biodiesel from palm oil sludge and palm kernel oil using non-heating method.

The specific objectives are: (1) Determination of the physico-chemical properties of palm oil sludge and palm kernel oil. (2) Production of biodiesel from palm oil sludge and palm kernel oil using non-

heating method (by agitation at room temperature); and the characterisation of the biodiesel so produced.

## MATERIALS AND METHODS

### Sample collection and preparation

The samples: palm oil sludge, black palm kernel oil (BPKO) and white palm kernel oil (WPKO) were collected from local oil millers in Okene, Kogi State, Nigeria, and transported to the laboratory in a clean 5-litre container. The samples were stored in a dry, clean and cool environment before pre-treatment.

### Pre-treatment of POS, BPKO and WPKO

The oil samples were heated gently at 15 ºC on a hot plate and filtered immediately using suction pump in order to remove the particles and dirt.

### Degumming

From each of the filtered oil samples, 800 ml were measured and heated in an oven set at 80 ºC for one hour. Exactly 8 ml of citric acid solution (2%) was added. The mixture was transferred into separating funnels and agitated for 20 minutes, then allowed to stand for 60 minutes. The gum was removed and the process was repeated with another 8 ml of citric acid solution. The oil was transferred to 1000 ml capacity beaker and left for 5 days for the water to evaporate until clear oils were obtained.

### Determination of physicochemical POS and PKO

Some physicochemical properties were determined using standard methods for both palm oil sludge and palm kernel oil. Properties measured included Acid value, Free Fatty acids (FFA), saponification value, Iodine value, specific gravity, peroxide value, and viscosity.

### Acid value and free fatty acid determination (% FFA)

Acid value was determined by ASTM method [9]. Degummed oil sample (1.0 g), was weighed into 250 $cm^3$ conical flask and 50 $cm^3$ of neutralized ethyl alcohol was added. The mixture was heated on a water bath to dissolve the sample. The solutions were allowed to cool and titrated against 0.1M potassium hydroxide using phenolphthalein indicator after which the acid value and free fatty acid was determined as follows:

$$\text{Acid value mg KOH/g oil} = \frac{56.1 \times C \times V}{\text{Weight of oil sample}}$$

Where, V= volume of the potassium hydroxide solution used, C = Molar concentration of potassium hydroxide solution used, 56.1 = Relative molar mass of potassium hydroxide, the acid value was obtained from free fatty acid determination as follow:

% Free Fatty Acid (FFA) = Acid Value × 0.503

**Saponification value determination [10]**

The degummed sample oil (2.0 g) was weighed accurately and dissolved 25 $cm^3$ of 0.5M alcoholic potassium hydroxide solution in a 250 $cm^3$ conical flask. A reflux condenser was fitted to the flask and heated in a water bath for an hour, swirling the flask frequently to ensure that the sample was dissolved. The excess KOH solution was titrated hot with 0.5M HCl solution using 1 $cm^3$of phenolphthalein indicator until a pink colour was observed. A blank determination was also carried out. The Saponification value was estimated using:

$$\text{Saponification value mg KOH/g oil} = \frac{56.1 \times C \times (V_0 - V)}{M}$$

Where: V = Volume 0.5 M HCl solution used for the blank titration, Vo = Volume of 0.5 M HCl solution used for the titration of sample, M = M in gram of oil used, C = Molar concentration of HCl solution used, 56.1 = relative molar mass of KOH

**Determination of iodine value [11]**

The oil sample (1.0 g) was weighed into conical flask and 25 $cm^3$ of carbon tetrachloride was added to dissolve the oil. Wijj's Reagent (25 $cm^3$) was added to the flask using a measuring cylinder in a fume chamber. Stopper was moistened with potassium iodide and then inserted and the content of the flask was vigorously swirled. The flask was then placed in the dark for 30 minutes. At the end of this period, 20 $cm^3$ of 10% aqueous potassium iodide and 100 $cm^3$ of water were added using a measuring cylinder. The content was titrated with 0.1M sodium thiosulphate solution. Few drops of 1% starch indicator were added and the titration continued by adding the sodium thiosulphate drop wise until coloration disappeared after vigorously shaking. The same procedure was used for the blank titration without the oil. The Iodine value was determined using the formula:

$$Iodine\ value\ (IV) = \frac{12.69 \times C \times V_2 - V_1}{Weight\ of\ sample\ (g)}$$

Where: C = concentration of sodium thiosulphate solution used, $V_1$ = volume of sodium thiosulphate used for sample, $V_2$ = volume of sodium thiosulphate used for blank, 12.69 = Constant.

**Determination of peroxide value [11]**

The oil sample (5.0 g) was dissolved in a solution containing 5.0 g of potassium iodide powder in 20 $cm^3$ of glacial acetic acid – chloroform mixture (3:2) v/v in a 250 $cm^3$ conical flask. Distilled water (35 $cm^3$) was added to the solution followed by a vigorous agitation. The solution was warmed on a water bath for 30 seconds after which 35 $cm^3$ of distilled water was added, agitated vigorously and the free iodine liberated was titrated with 0.1M solution of sodium thiosulphate using 1 $cm^3$ of starch indicator until the end point is attained (blue colour disappears). Blank was also prepared and titrated as above. The peroxide value was obtained using equation of the formula:

$$\text{Peroxide value meq/kg oil} = \frac{(V - V_0) \times C \times 12.69}{Weight\ of\ sample}$$

Where: V = Volume of Sodium thiosulphate solution used for sample titration, $V_O$ = Volume of Sodium thiosulphate solution used for the blank titration, W = Weight of sample (g), C= molarity of sodium thiosulphate solution.

**Determination of specific gravity [12]**

A clean and dry empty stoppered density bottle of 25 $cm^3$ capacity was weighed and the weight recorded as $W_o$. The density bottle was then filled with distilled water, stoppered and maintained in a water bath at 15°C for 10-15 min for the water to assume the bath temperature. The outside of the bottle was wiped, dried and reweighed as $W_1$. The bottle was emptied, washed with water and dried. It was then filled with the oil and equilibrated to 15°C in the water bath. The outside of the bottle was again wiped dry and weighed as $W_2$. The specific gravity of each sample was extrapolated using the equation:

$$Specific\ gravity\ at\ 15^0C = \frac{(W_2 - W_0}{(W_1 - W_0)}$$

Where: $(W_2 - W_o)$ = Mass of sample, $(W_1 - Wo)$ = Mass of an equal volume of water

**Viscosity**

Viscosity of sample oil was carried out at the Department of Chemical Engineering, Ahmadu Bello University, Zaria, using Brookfield Synchro Electric Viscometer. It estimated the value of the viscosity of liquid by placing a sensitive spindle of the device into the sample oil in a 100 ml beaker and getting the reading on the meter.

**Production of biodiesels**

The production of biodiesel from POS and PKO was carried out in two main steps: Esterification step (Reduction of high Free Fatty Acids) and Trans-esterification step. In esterification, methanol (150.0 g) and 5.0 g of concentrated sulphuric acid (analytical grade) were added to 500.0 g of the pre-treated oil at 60 ºC. The mixture was stirred for 60 minutes and allowed to stand in a separatory funnel [13]. The methanol-water mixture was decanted, the oil layer then removed and tested for acid value. This process was repeated until the FFA reduced to 0.5%. In trans-esterification, methoxide (catalyst) was prepared by dissolving 8.1 g of potassium hydroxide (analytical grade) in 90.265 $cm^3$ of methanol (85%) in a 250 $cm^3$ conical flask and then stored in a well-sealed container. Solution prepared as stated above (72.20 $cm^3$) which is 80% was added to 500 g of sample oil in a 1.5 litre glass blender. The mixture was reacted together for 5 seconds per 15 minutes for an hour at room temperature in the closed vessel. The resulting mixture was transferred into a separatory funnel and allowed to stand for 3 hours. The glycerol at the base of the funnel was then tapped off and the remaining liquid (biodiesel) was returned back to the blender for further trans-esterification with 18.05 $cm^3$ (20%) of methoxide. After complete reaction, the mixture obtained was allowed to stand in a separatory funnel again to further separate any remaining glycerol [14].

**Biodiesel purification (washing and drying)**

The biodiesel obtained above was washed with equal volume of water in a separatory funnel by gently swirling the funnel and then allowed to stand for the water to settle at the bottom. The water was then removed and the process repeated for five (5) times. Thereafter, the biodiesels obtained were left in wide open containers to dry for five (5) days.

**Determination of fuel properties**

Some physicochemical properties were determined using standard methods for both palm oil sludge and palm kernel oil methyl esters. Properties measured included: acid value, specific gravity, viscosity, flash point, cetane number, cloud point, pour point, sulphur content and ash content using ASTM methods.

**Determination of Fatty Acid Composition**

The gas chromatographic analysis of the POS and PKO and their respective biodiesels was made using Agilent 7890A series chromatograph equipped with Mass Spectrometer detector (model No. 5975). For the ester concentration of the biodiesels to be analyzed, the gas chromatograph was equipped with a capillary column of dimension 30 m x 250 um x 0.25 µm packed with non-polar HP-5. The column temperature was programmed initially at 100 ºC for 20 min, and then increased to 180 ºC at the rate of 10 ºC/min, for 10 min and then increased to 290 ºC. The inlet temperature was set at 300 ºC. Acquisition was carried out using SCAN mode [15].

**RESULTS AND DISCUSSION**

**Physicochemical properties of palm oil sludge and palm kernel oil**

The physicochemical properties of palm kernel oil (black and white) are presented in Table 1. The result shows significant differences among all the physicochemical properties examined.Acid value (78.877±0.04 mg KOH/g), free fatty acid (39.44±0.02%), specific gravity (0.884±0.01 g/cm$^3$) and ash content (0.01±0.001%) were significantly higher for palm oil sludge. Saponification value (258.96±0.060 mg/g), iodine value (36.32±0.200 g/g) and specific gravity (0.884±0.001 g/cm$^3$) were higher for black palm kernel oil while peroxide value was highest for black palm kernel oil with value of 1.40±0.020 meq O$^2$/kg.

Plant oils generally have specific gravity of 0.820 to 1.071 at 30 ºC and are considered good for biofuels production [16, 17]. The specific gravity of the palm oil sludge, the white palm kernel and the black palm kernel oils were 0.884, 0.881 and 0.884 respectively. The POS and BPKO had the same value and significantly different from WPKO. This may be due to the presence of impurities in the production of the POS and the BPKO.

The acid number is a direct measure of free fatty acids. It is expressed as mgKOH/g. The free fatty acid values for POS, WPKO and BPKO were 39.44%, 4.39% and 3.55% respectively. The POS is seen to be higher when compared with the PKOs which may be simply due to its

exposure in open ponds which makes them susceptible to oxygen damage. This occurs when the biochemical reaction between fats and oxygen cause the degradation of long chain fatty acids to short chain fatty acids and butyric acid, thereby increasing the acid value [18]. Chow and Ho [19] also reported that the free fatty acid content in POS varies depending on its exposure time. The three oil samples were subjected to heat during extraction and this could lead to high acid value observed in them suggesting the need for pretreatment before converting it to biodiesel. This is above the ASTM established standard of <0.5 mgKOH/g FFA.

The saponification value reported for POS (212.6 mg/g), WPKO (253.29 mg/g) and BPKO (258.96 mg/g) were high. This therefore indicates the presence of high percentage of fatty acids which might lead to soap formation [20], hence the separation of biodiesel and glycerin will be very difficult. Soap inhibits the separation of biodiesel and glycerin fraction and this could account for the low yield of biodiesel product (86-89 %) as against the standard yield of 96% reported by Stavarache *et al*. [21]. High amount of soap can result in irregular combustion and thick exhaust smoke but would also increase the cleanliness of the fuel internal components and reduce friction between rubbing parts. The result also shows that white (253.29 mg/g) and black PKO (258.96 mg/g) saponification values were higher than POS (212.60 mg/g) accounting for higher saturated fatty acids seen or observed in their fatty acid methyl ester profile and lower percentage yield of their methyl ester white palm kernel oil methyl ester (WPKOME) had 80.10% and black palm kernel oil methyl ester (BPKOME) had 81.53% when compared with palm oil sludge methyl ester (POSME) with percentage yield of 89.08. Anon [22] stated that saponification value will be higher if the oil contains more of saturated fatty acids (C14:0, C16:0, C18:0). Ankapong [23] also reported 201 mgKOH/g and 247 mgKOH/g for palm oil (PO) and palm kernel oil (PKO) respectively in his work.

The iodine value (IV) measures the unsaturation of fats and oils. High iodine value indicates high unsaturation of fats and oils [24, 25]. The iodine value observed in this work were 32.74, 13.33 and 36.32 $mgI_2/g$ for POS, WPKO and BPKO respectively indicating the presence of small number of C=C bonds in the oil as a result of high degree of saturation. The wide difference observed in WPKO and BPKO may be due to extraction method, as they are expected to have a very close value. Anon [22] stated that iodine value should be less than 115 based on ASTM biodiesel standards. So, values obtained in this work indicate that these oil sources may be

qualified for the production of bio-diesel. These values quantify the amount of double bond present in the oil and consequently reflecting the susceptibility of oil to oxidation.

Peroxide value of POS, WPKO and BPKO were 0.70, 1.00 and 1.40 (meq $O_2$/kg) respectively. The maximum level suggested by FAO of United Nation [26] is up to 10 milli equivalents of active oxygen/kg oil in refined oil. According to Gunstone [27], freshly refined oils regularly have a peroxide value, lower than 1 meq/kg oil and oil is considered to be rancid at a peroxide value above 10 meq $O_2$/kg oil and 1.52 (meq $O_2$/kg) for POS. The peroxide value of the oil used in this work were within the level suggested by FAO indicating the three oils are good for biodiesel production.

Biodiesel exhibits specific gravity between 0.86 – 0.90 depending on the feed-stock used. The specific gravity of the methyl esters of POS, WPKO and BPKO (Table 2) were within the stipulated limits of 0.90 for fuel grade biodiesel and conventional diesel. On transesterification, the specific gravity was reduced from 0.884 to 0.871 in POSME, from 0.881 to 0.871 in WPKOME and finally from 0.884 to 0.871 in BPKOME. Biodiesel with high density means more mass per unit volume of fuel which makes more energy available for work output. The petroleum diesel used recorded 0.8786.

Table 1: Physicochemical Properties of Palm Oil Sludge and Palm Kernel Oil

| **Property** | **POS±SD** | **WPKO±SD** | **BPKO±SD** |
|---|---|---|---|
| Acid Value (mg KOH/g) | $78.877^{a}$±0.04 | $8.799^{b}$±0.001 | $7.106^{c}$±0.101 |
| Free Fatty Acid (%) | $39.44^{a}$±0.02 | $4.39^{b}$±0.010 | $3.553^{c}$±0.002 |
| Saponification Value (mg/g) | $212.6^{c}$±0.20 | $253.29^{b}$±0.300 | $258.96^{a}$±0.060 |
| Iodine Value (g/g) | $32.74^{b}$±0.10 | $13.33^{c}$±0.030 | $36.32^{a}$±0.200 |
| Specific Gravity (g/cm$^3$) | $0.884^{a}$±0.01 | $0.881^{b}$±0.001 | $0.884^{a}$±0.001 |
| Peroxide Value ((meq $O_2$/kg) | $0.70^{c}$±0.02 | $1.00^{a}$±0.050 | $1.40^{b}$±0.020 |

$^{abc}$Means with different superscripts are significantly different, SD=Standard Deviation, POS=palm oil sludge, WPKO=white palm kernel oil, BPKO=black palm kernel oil.

**Fuel properties of palm oil sludge, palm kernel oil and petroleum diesel**

The fuel properties of palm oil sludge, palm kernel oil and petroleum diesel is presented in Table 2. The result shows that flash point, colour, cloud point, pour point, acid value, cetane number and free fatty acids were significantly higher ($p<0.05$) for palm oil sludge with values of 111±1.00,

3.50±0.10, 13.00±0.20, 10.00±0.20, 1.12±0.001, 49±0.20 and 0.56±0.01 respectively. Petroleum diesel had the highest viscosity value (6.72±0.01), sulphur content (0.1521±0.002) and specific gravity (0.878±0.001). White palm kernel oil (WPKO) and black palm kernel oil (BPKO) were statistically similar ($p>0.05$) and least for almost all the parameters measured.

The cetane numbers of the biodiesels produced from the POS (49), white (48) and black PKO (48) are in the medium range indicating good ignition and combustion quality of the fuels. These values are little above or close to the minimum limits of 47 and 51 prescribed in ASTM D6751 and EN 14214 respectively. The cetane number of the POS, WPKO and BPKO methyl ester exceeds the minimum value of 47 prescribed by ASTM D6751 and is higher than that of fossil diesel which was 41. Bangboye and Hansen [28] observed that feedstocks with high saturated fatty acids will have high cetane number, while those high in unsaturated fatty acid have lower cetane number (20-40). This implies that the oils used are higher in saturated fatty acids, hence, increases the stability of the biodiesels.

The results obtained for pour point of methyl estersare all within the range specified by ASTMD 6751 (-15 to 16 $^{o}$C). They are therefore safe in term of its flow characteristic hence engine cannot be clogged [29]. The petroleum diesel used shows a pour point temperature of 0 $^{o}$C which is higher than the value specified by ASTM 975 for petroleum diesel (-35 to -15 $^{o}$C).

The result shows the cloud point of POS methyl ester (13 $^{o}$C) to be higher than PKO methyl esters (5-7 $^{o}$C). This observation in POS biodiesel is expected because of the high composition of oleic acid present in the methyl ester which enhances cloud point [30]. Generally, a fuel with high cloud point is often limited in its use as fuel in cold climates. The high content of Oleic acid results in poor cold flow properties of Palm biodiesel. Nevertheless, the results were within the range of ASTMD 6751 that registered -3 to 12 $^{o}$C, except that of POSME which was slightly higher.

The difference in kinematic viscosity values of these biodiesels may be attributed to their different fatty acid compositions [31]. The viscosity of POSME (4.90 $mm^2/s$) was higher than that of WPKOME (3.24 $mm^2/s$) and BPKOME (3.21 $mm^2/s$) suggesting that POSME contains higher amount of fatty acid. According to ASTM D 6751(08) and EN 14214(03), for biodiesel to be used in diesel engines, the kinematic viscosity must be between 1.9 and 6.5 $mm^2/s$ and 3.50 and 5.0 $mm^2/s$ respectively. Viscosity increases with chain length (number of carbon atoms) and with increasing degree of saturation. On the other hand, viscosity is inversely related to the number of double bonds. The kinematic viscosity reported for the biodiesel produced from POS and PKO are

within specified range by ASTMD 6751 and EN1421, meaning that they will burn completely causing no deposit formation in the fuel injector of diesel engine [32]. The amount of saturation is higher in PKOMEs. Therefore, it is expected to observe higher viscosity than in POSME but the reverse is the case. This might be caused by the method employed in the transeterification process, thus POS is affected. The presence of oleic acid as unsaturated methyl ester has contributed to the good viscosity of the methyl ester of the three oil samples. In addition, presence of multiple bonds imparts low viscosity to biodiesel.

Flash point measures flammability of fuels and making it an important safety criterion in transportation and storage. In this research POSME had the highest flash point with 111 $^{o}$C while WPKOME had 105 $^{o}$C. These values are within the ASTM standard for biodiesel which allows the range of 100-170 $^{o}$C except BPKOME that had 85 $^{o}$C which was below the standard. Petroleum diesel used in this research showed a flash point of 95 $^{o}$C, higher than the ASTM standard of 60 – 80 $^{o}$C for diesel fuel. POS biodiesel with higher flash point has the advantage of increased safety, ease of transport and safe storage compared to fossil diesel.It also has lower fire risk and reduced chances of uncontrolled detonation [33].

The biodiesel samples in this research showed acid values of 1.12 mg KOH/g for POSME, 0.66 mg KOH/g for WPKOME and 0.44 mg KOH/g for BPKOME samples as shown in Table 2. The slight difference in the PKOMEs may be due to the method of extraction of the oil before converting it to biodiesel. Though the values obtained were within the range of the ASTM D664 which allows a specified maximum limit of 0.80 mg KOH /g for biodiesels, POSME value is higher (1.12 mg KOH/g) indicating that lipid deterioration reaction had occurred in palm sludge oil. The acid number of biodiesels depends on the fatty acid content of the feedstock used. From the literature, palm oil contained 41.00% mono-unsaturated fatty acids while palm kernel oil contains 14.00%, which may be responsible for the high acid number in some of their biodiesels. The low acid values in these fuels will not pose any threat to the engine's operating components, especially the fuel injection equipment. The European and American standards specify a maximum value of 0.5 mg KOH/g and 0.8 mg KOH/g of sample respectively. There was appreciable reduction in percentage free fatty acid of the biodiesels compared to their oils, as high proportion of the FFA was neutralized by potassium hydroxide during transesterification [34].

The sulphur content of the biodiesel (methyl ester) obtained from POS, WPKO, and BPKO were 0.0133, 0.0197 and 0.0378 % w respectively. The petroleum diesel used registered 0.1521 %

w and they are all within the standard limit set by ASTMD 6751 (0.05 %). It was observed that the petroleum diesel had a higher value than biodiesel confirming the report of William [35] that biodiesel has lower sulphur content when compared to petroleum diesel. This will make its combustion products to contain high oxides of sulphur, which has the potential to dissolve in water to form sulphuric acid and eventually cause corrosion of metals [36]. On the other hand, the combustion of POS methyl ester and PKO methyl esters will therefore yield products with low oxides of sulphur making it more environmentally friendly than fossil diesel.

EN 14214 (2003) and ASTM 6751 (2003) had established a maximum value of 0.02% for sulphated ash. This property is important since high values are generally associated with coking of injectors and clogging of fuel filters [23].

Table 2: Fuel Properties of Palm Oil Sludge, Palm Kernel Oil Methyl Esters and Petroleum Diesel

| **Property** | **POS Methyl Ester±SD** | **WPKO Methyl Ester±SD** | **BPKO Methyl Ester±SD** | **Petroleum Diesel ±SD** |
|---|---|---|---|---|
| Flash Point ($^oC$) | $111^a$±1.00 | $105^b$±0.50 | $85^d$±0.10 | $95^c$±0.20 |
| Viscosity ($mm^2/s$) | $4.90^b$±0.10 | $3.24^c$±0.04 | $3.21^c$±0.01 | $6.72^a$±0.01 |
| Cetane Number | $49^b$±0.20 | $48^b$±0.50 | $48^b$±1.00 | $44^a$±1.00 |
| Cloud Point ($^oC$) | $13.00^a$±0.20 | $7.00^d$±0.10 | $5.00^c$±0.01 | $6.00^b$±0.10 |
| Pour Point ($^oC$) | $10.00^a$±0.20 | $-9.00^d$±0.01 | $-3.00^c$±0.01 | $0.00^b$±0.00 |
| Sulphur (%) | $0.0133^d$±0.001 | $0.0197^c$±0.001 | $0.0378^a$±0.01 | $0.1521^b$±0.002 |
| Specific Gravity ($g/cm^3$) | $0.871^b$±0.001 | $0.871^b$±0.02 | $0.871^b$±0.01 | $0.878^a$±0.001 |
| Acid Value (mg KOH/g) | $1.12^a$±0.001 | $0.66^b$±0.002 | $0.44^c$±0.002 | - |
| Ash Content (%) | $0.01^a$±0.001 | $0.00^b$±0.00 | $0.01^a$±0.0005 | - |
| Moisture content | 0.01±0.00 | 0.01±0.00 | 0.01±0.00 | 0.01±0.00 |

$^{abc}$Mean with different superscripts are significantly different, SD=Standard Deviation, POS ME=palm oil sludge methyl ester, WPKO ME=white palm kernel oil methyl ester, BPKO ME=black palm kernel oil methyl ester.

The result showed that the ash contents of the methyl esters from the three-oil used were low. These agreed with the fuel specifications, almost nothing, indicating no abrasive solid, catalyst residues and soluble metal soaps concentrate in the biodiesel fuel that can form ash when oxidized during the process of combustion, therefore no engine deposits.

The water content in the biodiesel from POS, WPKO and BPKO were the same 0.01% meaning no water contaminant in the fuel that could result in engine corrosion or react with the glycerides to produce soaps and glycerine. EN 14214 (2003) imposes a maximum content of 0.05% of water in fuels. This proves that the technique used in drying the biodiesels is effective, cheap and simple (mere exposure to air overnight).

**Fatty acid profile of palm oil sludge and palm kernel oils methyl esters**

Tables 3-5 show the GCMS of the fatty acid profile of the biodiesels. The result obtained shows that POSME contained 58.23% oleic acid and 38.48% palmitic acid as the major fatty acids present. Whereas WPKOME revealed 18.10% oleic acid, 8.98%, palmitic acid, 26.65% lauric acid and 18.65% myristic acid methyl ester as the major fatty acids' methyl ester present in WPKOME. BPKOME also had the same major fatty acids with oleic acid of 23.82%, palmitic acid 11.98%, lauric acid 30.93% and myristic acid methyl ester 23.23%. It was observed that 3.70% stearic acid methyl ester (C18:0) was present in BPKOME and none in the WPKOME. This could be due to the method of extraction. The POSME contained high amount of oleic acid (C18:1), mono unsaturated fatty acid and palmitic acid when compared with white and black PKOME. From the table of result, it was observed that WPKOME and BPKOME had more saturated fatty acids than the POSME. The high percentage of the saturated fatty acid in WPKOME and BPKOME and monounsaturated fatty acid in POSME is an indication of high heat of combustion which would be readily released during combustion [36]. This property compliments other properties such as specific gravity, peroxide value and iodine value to make it a good potential for biodiesel production [37]. The low iodine value in POS (32.74 g/g) gave rise to high amount of unsaturation of ester (58.62%) seen in POSME. The iodine value of the three-oil recorded in Table 1, was responsible for the variation in level of unsaturation (C18:1) observed in the biodiesel produced from these three oils.

Oleic acid is a desirable fatty acid among the other common fatty acids to enrich or improve the fuel properties of biodiesel [38]. The quality of the fuel is therefore a reflection of the composition of the oleic acid in the oil. Oleic acid, a monounsaturated fatty acid was a significant contributor to the quality of palm oil sludge methyl ester and palm kernel oil methyl ester. Palmitic acid also contributed significantly to the quality of biodiesel. The fatty acid composition of POS methyl ester (99.88%), WPKO methyl ester (76.27%) and BPKO methyl ester (99.19%). Here the

composition of POSME and BPKOME were above the 96.5% minimum specified by EN Standard for ester content. This is an indication that they are very good as biodiesel fuel and the non-heating method adopted in the production process, yielded good effect on the ester content. However, the percentage composition of WPKOME was lower than BPKOME irrespective of the same conditions they were subjected to during transesterification process. This may be due to the method of their extraction. It was also discovered that the oleic acid present in the POSME was higher than that seen in the PKOMEs making POSME more preferred as biofuel since Oleic acid (monounsaturated methyl ester) is a good compound with respect to stability of the biodiesel as higher degree of unsaturation in the fatty acid methyl esters limits its suitability for use as a fuel due to high polymerization tendency as a result of peroxidation [39]. The limitation of unsaturated fatty acids is necessary due to the fact that heating higher unsaturated fatty acids results in polymerization of glycerides. This can lead to the formation of deposits or to deterioration of the lubricants [40].

Table 3: Major Resolved Peak Areas of Biodiesel from POS Gas Chromatogram and their Suggested Compounds from NIST14 Library

| Peak no. | Area% | Compound | Corresponding Structure |
|---|---|---|---|
| 1 | 0.16 | Dodecanoic Methyl Ester | $C_{12}$:0 |
| 2 | 1.28 | Methyl tetradecanoate | $C_{14}$:0 |
| 3. | 0.06 | Pentadecanoic Acid Methyl Ester | $C_{15}$:0 |
| 4. | 0.12 | 7 – Hexadecenoic Acid Methyl Ester | $C_{16}$:1 |
| 5. | 38.48 | Hexadecanoic Acid, Methyl Ester | $C_{16}$:0 |
| 6. | 0.16 | Heptadecanoic Acid, Methyl Ester | $C_{17}$:0 |
| 7. | 58.23 | 9-octadecenoic Acid, Methel Ester | $C_{18}$:1 |
| 8. | 0.39 | Cis-13- Eicosenoic Acid Methyl Ester | $C_{20}$:1 |
| 9. | 0.92 | Eicosanoic Acid Methyl Ester | $C_{20}$:0 |
| 10 | 0.20 | Docosanoic Acid Methyl Ester | $C_{22}$:0 |

Table 4: Major Resolved Peak Areas of Biodiesel from WPKO Gas Chromatogram and their suggested Compounds from NIST14 Library

| Peak no. | Area% | Compound | Corresponding Structure |
|---|---|---|---|
| 1 | 1.61 | Octanoic Acid Methyl Ester | $C_8$:0 |
| 2 | 2.19 | Decanoic Acid Methyl Ester | $C_{10}$:0 |
| 3 | 26.65 | Dodecanoic Acid Methyl Ester | $C_{12}$:0 |
| 4 | 18.65 | Methyl tetradecanoate | $C_{14}$:0 |
| 5 | 8.98 | Hexadecanoic Acid Methyl Ester | $C_{16}$:0 |
| 6 | 18.10 | 9 – octadecenoic acid Methyl Ester | $C_{18}$:1 |
| 7 | 0.06 | Eicosanoic acid Methyl Ester | $C_{20}$:0 |

Table 5: Major Resolved Peak Areas of Biodiesel from BPKO Gas Chromatogram and their suggested Compounds from NIST14 Library

| Peak no. | Area% | Compound | Corresponding Structure |
|---|---|---|---|
| 1 | 2.10 | Octanoic Acid Methyl Ester | $C_8$:0 |
| 2 | 3.37 | Decanoic Acid Methyl Ester | $C_{10}$:0 |
| 3 | 30.93 | Dodecanoic Acid Methyl Ester | $C_{12}$:0 |
| 4 | 23.23 | Methyl tetradecanoate | $C_{14}$:0 |
| 5 | 11.93 | Hexadecanoic Acid Methyl Ester | $C_{16}$:0 |
| 6 | 23.82 | 9- Octadecenoic Acid Methyl Ester | $C_{18}$:1 |
| 7 | 3.72 | Methyl Stearate (methyl octadecanoate) | $C_{18}$:0 |
| 8 | 0.09 | Eicosanoic acid Methyl Ester | $C_{20}$:0 |

## CONCLUSIONS

The following conclusions were made from this study: The physicochemical properties of the oil determined were within the accepted limits for biodiesel production except the acid values that were high and pretreatment was carried out to reduce it. The GCMS of the fatty acid methyl esters showed fatty acid profiles rich in palmitic, and oleic acids indicating that these FAMEs can serve as fossil diesel substitute. Biodiesel can be produced effectively by agitation of the feedstock at room temperature thus reducing the cost of production where heating was required.

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