



## SOME CHEMICAL PROPERTIES of FATTY ACID PROPYL ESTERS (BIODIESEL) PRODUCED VIA TRANSESTERIFICATION of OIL SEED CROPS

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### ABSTRACT

The global interest in renewable combustibles has been seriously intensified nowadays, mainly due to worldwide energy crises; including high energy demand, pollution problems, instability and fluctuating oil price, reduction of the availability of fossil fuels, increasing energy subsidies and impact on the ecology. Biodiesel are biofuels produced from biomass which are clean alternatives fuels. Biofuels synthesis from biomass is of interest because these biomasses are renewable, biodegradable, readily available and environmentally benign resources. This work reports the results of the study of some chemical properties and analysis of biodiesel produced from Castor (CSO), Palm kernel (PKO) and Groundnut (GNO) oils. The biodiesel was produced by transesterifying refined oil samples (CSO, PKO and GNO) at 6:1 1-propanol to oil molar ratio in the presence of their various optimal catalyst weight earlier calculated (0.50 wt/v for CSO and PKO, and 0.40 wt/v for GNO) at 65°C for 60 minutes. The process for the production of biodiesel using an alkali (sodium hydroxide – NaOH) catalyzed method in a batch reactor was composed of glycerol separation steps (after each transesterification step) and an ester purification step. The following values were obtained for CSO, PKO and GNO biodiesels: Saponification value 168.20, 204.50 and 180.08 mg KOH/g; acid value 0.44, 0.48 and 0.52 mg NaOH/g; iodine value 71.01, 12.11 and 74.05 g I<sub>2</sub>/g which were within Biodiesel standards EN 14214(Europe) ASTM D 6751 (America) for Vehicles utilizing biodiesel. The infrared spectra results revealed the presence of major functional groups in the three oils, obviously hydroxyl (3445.51cm<sup>-1</sup> for CSO, 3466.43 cm<sup>-1</sup> for GNO and 3459.87 cm<sup>-1</sup> for PKO); carbonyl (1746.70 cm<sup>-1</sup> for CSO, 1744.95 cm<sup>-1</sup> for GNO and 1746.67 cm<sup>-1</sup>); Olefinic (1652.01 cm<sup>-1</sup> for CSO, 1652.71 cm<sup>-1</sup> for GNO and 1644.83 cm<sup>-1</sup> for PKO) and methylenic (2925.73 cm<sup>-1</sup> for CSO, 2924.89 cm<sup>-1</sup> for GNO and 2924.03 cm<sup>-1</sup> for PKO). Generally, results obtained were within acceptable range set by various International Standards, showing promising sources for biodiesel production in Nigeria.

**Keywords:** Biodiesel, Transesterification, Alkali-catalysis, Infrared, Renewable.

### INTRODUCTION

Much academic researches explore new ways to create greener and environmentally friendlier biofuel from bioenergy crops that are renewable, because fossil fuels (petroleum, diesel, coal e.t.c.) will not last forever, coupled with its rising cost and combustion generated pollutants

in the form of carbon dioxide, along with other greenhouse gases, such as nitrous oxide and methane, leading to planetary warming impact (Demirbas, 2009; Marchetti and Errazu, 2010; Madarasz and Kumar, 2011; Vashist and Ahmad, 2011; Lin *et al.*, 2012; Shrestha, 2013).

Available statistical data ranked Nigeria (as at beginning of 2017) as the second largest oil producing country in Africa and the 11<sup>th</sup> largest oil producing country in the world (EIA, 2017). This amazing oil wealth notwithstanding, the Energy Commission of Nigeria (ECN) expressed fears over future depletion of these fossil fuels

and the severe environmental impacts. It has also been reported that the major oil fields from the twenty largest world oil producers are already experiencing decline in oil reserves and some have been producing near their peak rate (Russia, Saudi Arabia and the United States)

**Table 1: World oil Producers with declining / static oil reserves by ranking**

Country	Oil (millions of barrels) MMbbl	
	Year end 2015	January 1, 2017
Venezuela	300,900	300,878
Saudi Arabia	266,600	266,455
Canada	172,200	169,709
Iran	158,800	158,400
Iraq	143,100	142,503
Kuwait	101,500	101
UAE	97,800	97,800
Russia	102,400	80,000
Libya	48,400	48,363
United States	55,000	39,230
Nigeria	37,100	37,062
Kazakhstan	30,000	30,000

Source: EIA, (2017)

Biodiesel is an alternative to petroleum based fuels derived from plant oils, used waste cooking oil and animal fats (Balat and Balat, 2008; Lateef *et al.*, 2014) obtained through the process of transesterification ( Baroi *et al.*, 2009; Tavlarides *et al.*,2010). Experimentally, the process takes place in the presence of linear/monohydric alcohols (alcoholysis - methanol, ethanol, 1-propanol) (Sharma *et al.*, 2008, strong bases (NaOH, KOH or alkoxides), acid / base or enzymes catalysts at a lower temperature and pressure or in the absence of catalysts at a higher temperature and pressure. Biodiesel production is always associated with glycerol as by-product, also the base catalyzed transesterification process is faster than the acid catalyzed reaction, most commercial processes use a homogeneous base, i.e NaOH, KOH, or related alkoxides for biodiesel production (Gerpen, 2005; Lateef, 2010). Advantages of biodiesel over petro diesel includes biodegradability, higher flash point, inherent lubricity, low toxicity, negligible sulphur

content, and lower exhaust emissions (Moser, 2009; Bello *et al.*, 2012).

Vegetable oil is an important renewable feedstock in the long-term (2016-2025) vision of providing secure, abundant, cost effective and clean source of energy for Nigeria. Common vegetable oil in Nigeria include peanut (groundnut), soybean, cottonseed, palm oil, palm kernel, physic nut and castor. According to the United States Department of Agriculture, Recent statistical data (2017) ranked Nigeria to be the fourth and third world's largest producer of palm-kernel and groundnut oils respectively. It was also reported that castor oil plant originates in Africa and more importantly, it is a non edible oil. However, industrial use of these plants oil has been limited to soap, detergent, lubricants, paints e.t.c. This shows that despite the abundance of these plant oils, it has been underutilized in Nigeria. Successful reports on transesterification of some Nigerian oils in the preparation of biodiesel is an indication of better industrial utilization of these plant oils in Nigeria, as considerable research efforts are now

focusing on this alternative diesel fuel worldwide. ASTM specification for quality castor oil is presented in Table 1.

**Table 1: ASTM specification for quality Castor oil**

Property	Ranges	Selected
Specific gravity 20/25 <sup>0</sup> C	0.957-0.968	0.962
Refractive index	1.476-1.479	-
Saponification value	175-187	-
Un-saponification value	0.3-0.7	-
Iodine value	82-88	85
Hydroxyl value	160-168	160(min.)
Acid value	0.4-4.0	3

Source: Akpan *et al* (2006)

Biodiesel contains complex mixtures of fatty acids, lipids and esters, all of which possess a weak or no UV chromophore. Consequently, fatty acids and lipid are often derivatized to enhance their UV absorbance or to facilitate their detection by GC-MS. Such an approach is time consuming and difficult to apply to complex mixtures (Bullock, 2018). Spectroscopic methods are being increasingly utilized for quality control purposes (Knothe, 1999) and have been reported for the analysis of biodiesel / or monitoring of the transesterification reaction. Infrared provides a rapid, precise and accurate tool for biodiesel analysis (Bradley, 2007).

The absorption of electromagnetic radiation by some part of the molecule may be used to help gain precise information about structure. In the case of infrared (IR) spectroscopy, the radiation is passed through the sample under analysis and the spectrum is recorded. Molecules have different bond structures which absorb unique wavelength of light. IR measures how light interact with fuel components. The amount of light absorbed is proportional to that components concentration in the fuel. Infrared (IR) region produces primary absorbances that give fundamental knowledge of the types of chemical groups presents in the fuel. The benefits of IR spectroscopy include fast analysis, no waste chemicals, no consumables, portable/automated instruments. IR application for biofuel includes feedstock analysis, determination of product

blends, final product quality and contamination (Ritz and Nash, 2004).

Previous reports on transesterification of castor, palm-kernel and groundnut oils using methanol or ethanol as the alcohol in the preparation of biodiesel have proved successful (Alamu *et al.*, 2007; Nkafamiya *et al.*, 2010; Saliman *et al.*, 2010 Vashist and Ahmad, 2011; Pandurangan *et al.*, 2014; Olaniyi *et al.*, 2014; Mubofu *et al.*, 2015; Yusuf *et al.*, 2015 Oyerinde and Bello, 2016; Khaliq *et al.*, 2017). Therefore, the main objective of this work was to produce biodiesels from vegetable oils (Castor, Palm kernel and Groundnut oils) using 1-propanol as the alcohol through alkali-catalyzed process, characterize the biodiesels for chemical properties and to verify the applicability of infrared spectroscopy to gain fundamental knowledge of the type of chemical group present in the biodiesels.

## MATERIALS AND METHODS

Castor seeds, Palm kernel seeds and Groundnut seeds were obtained from Ogige market in Nsukka, Enugu State, Nigeria. The seeds were de-shelled by hand picking and the shell separated from the seed. The seeds were spread and dried under direct rays of sunlight (30<sup>0</sup>C) for three consecutive days. The solvents (n-hexane and absolute ethanol) from the three seeds (castor, palm-kernel and groundnut) were recovered with rotary evaporator (model ROTAVAPOR-R) and stored for further use at room temperature (30<sup>0</sup>C). All reagents used were

analytical grade, manufactured by Aldrich Chemicals.

Pre-treatment of oils, determination of optimal catalyst weight and alkali-catalyzed batch production of biodiesel was carried out as described by Lateef *et al* (2014).

#### **Pre-treatment of Oil Samples**

Three hundred milliliters of oil was heated with electric heater to 75°C in a 500 ml beaker. The oil was mixed with 0.1 % (v/v) of 85% phosphoric acid and distilled water to about 0.2 wt % of the oil. Magnetic stirrer was placed at the bottom of the 500 ml beaker to homogenize the oil for about 30 minutes. Gum which resulted from the homogenization was allowed to settle and the oil was decanted into another 500 ml beaker for refining.

In the refining step, temperature of the oil was restored to 75°C under a magnetic stirrer and 9.5wt% of NaOH solution was added gradually, as the mixture was continuously homogenized to convert the free fatty acids into soaps. 15 wt% distilled water of the total mixture was used to wash the oil free of soap in a 500 ml separating funnel. The washed oil was later dried at 105°C using oven (Labor Muszeripari) for 30 minutes.

#### **Determination of Optimal Catalyst Weight / Transesterification reaction**

Optimal catalyst weight tests were carried out on the pretreated oils in order to evaluate the amount of the alkali (NaOH) catalyst for the purpose of transesterification of the oils. Optimal catalyst weight was carried out as contained in the previous work (Lateef *et al.*, 2014).

The laboratory scale transesterification reactor (batch reactor) to produce propyl esters from castor oil, palm kernel oil and groundnut oil were carried out in a 200 ml conical flask (air-tight flask) and mounted on a magnetic stirrer. The magnetic stirrer was set to a constant speed throughout the experiment, to ensure uniform agitation and thorough homogenization of the reaction mixture.

Optimal catalyst tests were determined for each oil sample using 50 ml of the refined oils and the

volume of 1-propanol used on the basis of 3:1, 1-propanol to oil molar ratio. The catalyst used was sodium hydroxide (NaOH) pellet. The weights of the catalyst were varied from 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35 and 0.40 g.

NaOH pellets (as mentioned above) were dissolved in 15 ml of 1-propanol and the mixture stirred for 15 minutes to form sodium methoxide (CH<sub>3</sub>ONa) in an air-tight conical flask. This sodium methoxide was introduced gently into the heated oil in the reactor and the entire content was brought to a temperature of 55°C and then held at this temperature for 60 minutes. The reaction product mixture of the transesterification were allowed to separate into two phases by standing for 6 hours in a separating funnel (100 ml) so as to separate glycerol from the biodiesel. The two layers – superior (biodiesel) and inferior (glycerol) were separated by washing with warm distilled water to remove impurities. The denser soapy mixtures were carefully drained from the bottom of the 100 ml separating funnel, leaving behind the superior biodiesel layer. The volumes of the biodiesel obtained were determined in a measuring cylinder. A graph of biodiesel yield fraction against catalyst weight per volume of oil were estimated and plotted.

#### **NaOH-catalyzed Batch Production of Propyl esters (Biodiesel)**

The same procedure as contained in previous work (Lateef *et al.*, 2014) was adopted.

One hundred milliliters of the three oil samples was heated to 65°C and placed in a 250ml flat bottom flask-batch reactor (at 6:1 alcohol to oil molar ratio, 100ml of castor and palm kernel oil requires 60ml of 1-propanol and 100ml of groundnut oil requires 50ml of 1-propanol). The optimal catalyst (NaOH) earlier calculated for the three oils (0.50g for castor and palm kernel oils and 0.40g for groundnut oil) was dissolved into the alcohol by vigorous stirring in a separate air-tight container of 200ml. The alcohol-optimal catalyst weight mixtures were poured into the oils and the final mixture stirred vigorously for 60 minutes in an air-tight container.

### Separation of the Products

The product mixture was poured into a dry stoppered separating funnel of 500 ml volume. The reaction product mixture were allowed to separate into two phases at the end of the reaction; ester and crude glycerol, by standing for 15 hours in a separating funnel so as to separate glycerol from the biodiesel. The tap of the separating funnel was opened to evacuate the inferior layer (glycerol) and the crude biodiesel was left in the separating funnel.

### Biodiesel Washing and Drying

Fifty millimeter of warm distilled water at 45°C was used to wash the crude biodiesel thrice and dried in the oven at 105°C for 60 minutes. The volumes of the biodiesel obtained were recorded and samples were used for characterization.

### Characterization of the Crude and Refined Oils, Biodiesel

The reference methods for the characterization and examination of oils and biodiesels were carried out as described in [8] for saponification value (SV), iodine value (IV) and acid value (AV).

**Table 2: Yield of oils**

Sample	Weight of seeds (Kg)	Weight of extracted oil (Kg)	Percentage (%) yield
Castor seed oil	7.80	3.80	48.72
Palm kernel oil	6.56	2.78	42.38
Groundnut oil	8.10	3.76	46.42

The three oil samples showed good yield, with castor seed, having highest percentage (%) yield.

**Pre-treatment of Oils** Crude plant oils contain some free fatty acids and phospholipids. The

**Table 3: Percentage Loss on Pre-treatment of oils**

Sample	Weight of unrefined oil (kg)	Weight of refined oil (kg)	Percentage (%) loss on pre-treatment
Castor seed oil	3.80	3.58	5.78
Palm kernel oil	2.78	2.61	6.12
Groundnut oil	3.76	3.52	6.38

The free fatty acids and phospholipids are responsible for the significant losses recorded

### Infrared Spectroscopy-Biodiesel Product Analysis

Biodiesel produced at 65°C as outlined in using optimal catalyst weight were analyzed using Nicolet Avartar 310 FT-IR (Fourier Transform Infrared Spectrophotometer) equipped with KBr beam splitter. The smart ARK™ attenuated total reflection sensory was used to collect the data. About 0.4 ml of biodiesel samples were smeared to cover the sampling crystal. Spectra were collected in 40 seconds.

The data were collected using OMNIC™ spectroscopy software showing spectrum region, absolute threshold, sensitivity, peak list-positions (Figures 1-6).

## RESULTS AND DISCUSSION

### Extraction of Crude Plant Oils

The results of the yield of the oils, pre-treatment of the oils and percentage loss on pre-treatment of oils are reproduced as contained in previous work (Lateef *et al.*, 2014), for the purpose of better understanding of the feedstock properties.

three oil samples used for biodiesel production were, therefore pretreated to remove the free fatty acids and Phospholipids.

during pre-treatment. The oil extracted from groundnut has high acid values which could be

responsible for its high percentage loss during pre-treatment.

**Table 4: Result of the Optimal Catalyst Weight Test for Maximum Biodiesel Yield at 1:3 Oil/Alcohol Ratio**

Volume of oil (ml)	Volume of C <sub>3</sub> H <sub>2</sub> OH(ml)	CSO, PKO, GNO wt of catalyst (g)	% (wt/v) of catalyst	Vol. of Biodiesel			% yield of Biodiesel		
				CSO	PKO	GNO	CSO	PKO	GNO
50	15.00 for CSO & PKO and 12.50 GNO	0.05	0.10	4.1	7.0	1.5	8.2	14.0	3.0
50	15.00 for CSO & PKO and 12.50 GNO	0.10	0.20	6.0	18.0	19.5	12.0	36.0	39.0
50	15.00 for CSO & PKO and 12.50 GNO	0.15	0.30	19.0	33.0	35.0	36.0	64.0	70.0
50	15.00 for CSO & PKO and 12.50 GNO	0.20	0.40	30.0	38.0	39.6	60.0	76.0	79.0
50	15.00 for CSO & PKO and 12.50 GNO	0.25	0.50	33.0	39.5	34.0	66.0	79.0	68.0
50	15.00 for CSO & PKO and 12.50 GNO	0.30	0.60	12.5	37.5	38.5	65.0	75.0	57.0
50	15.00 for CSO & PKO and 12.50 GNO	0.35	0.70	31.5	36.0	25.0	62.5	72.0	50.0
50	15.00 for CSO & PKO and 12.50 GNO	0.40	0.80	29.5	25.0	15.0	59.0	50.0	30.0

#### Optimal Catalyst Weight Test

As evident From Table 4, weight of catalyst peaked steadily from 0.10% to 0.5% wt/v and thereafter, there were sudden and significant fall in the volumes of biodiesel for CSO and PKO; but GNO peaked at 0.4% wt/v but witnessed decrease thereafter. The percentage (%) of biodiesel from the oils are higher at this conditions -66.0,68.0 and 79.0 % for CSO, GNO and PKO respectively. It was actually confirmed during the experiment that increment in percentage weight per volume of the catalyst would not yield further volume increase in biodiesel obtained from castor seed, palm kernel

and groundnut oils. This observation was in agreement with Darnoko (2000) that, catalyst concentration levels greater than one may have favoured the backward reaction – the formation of glycerol. The optimal catalyst weight test is a simple test to confirm that increase in the amount of catalyst only lead to production of soaps and not biodiesel.

Different properties like saponification value (S.V), iodine value (I.V) and acid value (A.V) were determined for crude, refined oils and biodiesel produced from castor, palm kernel and groundnut oils.

**Table 5: Characterization of Crude/Refined Oils and Biodiesel**

Property	Crude oil	Refined oil	Biodiesel
Saponification value (mgKOH/g)			
CSO	183.70	181.00	168.20
PKO	242.80	238.00	204.54
GNO	189.70	182.30	180.08
Acid value (mgNaOH/g)			
CSO	3.02	0.74	0.44
PKO	3.04	0.79	0.48
GNO	3.78	0.52	0.52
Iodine value (g of I <sub>2</sub> /g)			
CSO	89.40	84.20	71.01
PKO	12.68	12.38	12.11
GNO	75.45	74.15	74.05

**Comparison with Biodiesel standards**

At 28°C, the acid value obtained for CSO and PKO falls within the limit specified by international standards. ASTM D 6751 (America), EN 14213 (Europe). Standard specify acid value ranges 0.50 maximum mg KOH/g or mg NaOH/g.

From the results of this study, the acid value of 0.44 and 0.48 mg NaOH/g at 28°C obtained for the CSO and PKO biodiesel agrees with standards ( as shown in Table 1) as its value falls within the recommended ranges. The acid value of GNO biodiesel 0.52 mg NaOH/g at 28°C is slightly higher by 0.02 by these two biodiesel specification standards, but less than Australian and Brazillian biodiesel standards ( acid number 0.80 mg KOH/g).

At 28°C, the iodine value obtained for CSO, PKO and GNO biodiesels falls within the limit specified for various international standards. EN 14213 (Europe), EN 14124 (Europe,) JIS K 0070 (Japan), EN 14111 (South Africa) standard specify iodine value 130,120, 140 g I/100g respectively for biodiesel fuel. From the results of this study, the iodine value of 71.01, 12.11

and 74.05 g I/100g were obtained for CSO, PKO and GNO biodiesels.

Furthermore, saponification value is not included in all the biodiesel quality standards, hence, there is no basis for comparison

**Characteristics of Crude and Refined CSO, PKO and GNO oils compared**

Characteristics of the oils were compared with oils of other countries and other geographical locations in Nigeria. The extracted oils were liquid at room temperature.

**Saponification value**

The saponification value of 183.70 mg KOH/g of crude CSO was lesser compared to 242.80 and 189.70 mg KOH/g of crude PKO and GNO respectively. The values reduced significantly when the oil samples were refined – 181.00, 238.40 and 182.30 mg KOH/g for CSO, PKO and GNO respectively. Saponification value and molecular weight are inversely related; high saponification value means low molecular weight of the triglycerides and vice-versa. From Table 5, it was shown that crude PKO recorded the highest saponification value while crude CSO had the lowest saponification value.

Saponification value of crude CSO and refined CSO (183.70 and 181.00 mg KOH/g) conformed to saponification value for ASTM specification (175-187 mg KOH/g) for quality Castor oil. Results obtained for both crude and refined CSO compare favourably with 182.96 mg/g in Salimat *et al.*, (2010) Malaysian castor oil; 185.83 and 181.55 mg NaOH/g of oil for both crude and refined CSO (Akpan *et al.*, 2006), Nigerian CSO; 181.52 mg KOH/g (AL-Harbawy *et al.*, 2014) Iraq CSO; 182.9 mg/g (Khaliq *et al.*, 2017) Nigerian CSO; but far from 76.68 – 80 mg KOH/g of oil for both crude and refined CSO (Mobufu *et al.*, 2015) Tanzanian CSO and 175.31(no unit) (Yusuf *et al.*, 2015) (though the value is still within ASTM Specification standards).

The Saponification value of 280.5 mg KOH/g reported by Olaniyi *et al* (2014) was higher compared to this study – 242.80 mg KOH/g and 238.40 mg KOH/g for crude and refined PKO respectively. Equally, Atasie and Akinhanmi (2009) reported 232.815 mg KOH/g for PKO.

In this study, Saponification value of GNO - 189.70 mg KOH/g and 182.30 mg KOH/g for both crude and refined GNO agreed closely with 190 mg KOH/g (Ozcan and Seven, 2003), Turkish (for crude GNO) and 189.90 mg KOH/g Pandurangan, Indian GNO. Nkafamiya *et al* (2010) reported 188-220 mg KOH/g and 179-184 mg KOH/g for crude and refined GNO in Nigeria. Saponification value of oil is one of essential parameters in determining the suitability of oil in soap making. Saponification value is a measure of the total free and combined acids in oil and fat and is defined as the number of milligram of potassium hydroxide required for the complete neutralization of the fatty acids of a sample (Pearson,1976).

### **Iodine value**

The iodine value (also known as iodine adsorption value or iodine number or iodine index) is the measure of the amount of unsaturation of the oil/ fatty acids. Table 5 presents a comparison between iodine values of

crude and refined Castor, Palm kernel and Groundnut oils. Significant differences are observed between the iodine value obtained for the crude and refined oils. Iodine value of 89.40, 12.69 and 75.45 g. I<sub>2</sub> for crude CSO, PKO and GNO; 84.20, 12.38 and 74.15 g. I<sub>2</sub> for refined CSO, PKO and GNO respectively (all below 100) were obtained, which suggests that the oil belongs to the class of non-drying oils, essential in the manufacture of soaps, lubricants and candle (Akpan *et al.*, 2006).

The iodine value of refined CSO in this study – 84.20 g of I<sub>2</sub>/g closely agreed with 84.50 mg/g Malaysian refined CSO as reported by Saliman *et al* (2010) and 84.80 g of I<sub>2</sub>/g Nigerian refined CSO reported by Akpan *et al* (2006).

The iodine value of 74.45 and 74.15 g of I<sub>2</sub>/g for both crude and refined GNO were less compared to 82 (no unit) and 95.300 (no unit) reported by Ozcan and Seven (2003) in Turkey and Panduranga *et al* (2014) in India respectively.

### **Acid value**

The acid values were lower than 1 mg NaOH/g for refined CSO, PKO and GNO – 0.74, 0.79 and 0.98 mg NaOH/g compared to crude CSO, PKO and GNO with values greater than 1 mg NaOH/g – 3.02, 3.04 and 3.78 mg NaOH/g. Thus there were corresponding low levels of free fatty acids in the refined oils, which also suggests low levels of degeneration in the refined oil. It is of importance to note that storage conditions and duration can equally affect the acid value of oils and fats.

The acid value reported for crude and refined CSO are within ASTM specification of quality Castor oil. The acid value of this study is in agreement with AL-Harbawy *et al* (2014) in Iraq and Khaliq *et al* (2017) in Nigeria.

Atasie and Akinhanmi (2009) reported a higher acid value of 11.60 mg KOH/g.

In this present study, the acid value of refined GNO -0.98 mg NaOH/g is in agreement with that of Ozcan and Seven (2003) -0.98 (no unit) in Turkey. Panduranga *et al* (2014) reported higher acid value 4.40 (no unit) in India.



The acid value is a measure of the amount of organic acids present in 1 g of the oils and fats (Conackci and Gerpen, 2001).

### **Infrared Spectroscopy-Biodiesel Product Analysis**

Fourier Transform Infrared (FT-IR) is a spectroscopic technique that is used to identify functional groups in different substances. In this work, FT-IR was used to identify functional groups in different oils - castor oil (CSO), groundnut oil (GNO), palm kernel oil (PKO) and their Fatty Acids Propyl Esters (biodiesel). The oils majorly contain saturated fatty acids and unsaturated fatty acids. The FT-IR spectra of CSO, GNO and PKO were analyzed in the 400-4000 $\text{cm}^{-1}$  range with FT-IR (310) Nicolet Avatar. The spectra are shown in Figure 1-6 and Table 6 shows the peaks identified from the spectra and their corresponding interpretations. The three oils (CSO, GNO and PKO) revealed similar major functional group absorption bands, notably for hydroxyl, carbonyl, Olefinic, methylenic etc groups and very few differential bands. The broad band peaking at 3445.51 $\text{cm}^{-1}$  for CSO, 3466.43  $\text{cm}^{-1}$  for GNO and 3459.87  $\text{cm}^{-1}$  for PKO represent O-H stretching vibration of alcohol hydrogen bond. The broad band area predicts prevalent concentration of O-H group of alcohol. Other well defined peaks are those for C=O stretching triglyceride ester linkage (1746.70  $\text{cm}^{-1}$  for CSO, 1744.95  $\text{cm}^{-1}$  for GNO and 1746.67  $\text{cm}^{-1}$  for PKO); C-H asymmetrical stretching ( $\text{CH}_2$ ) (2925.73  $\text{cm}^{-1}$  for CSO, 2924.89  $\text{cm}^{-1}$  for GNO and 2924.03  $\text{cm}^{-1}$  for PKO);  $\text{CH}_3$  bending (twisting) (1456.02  $\text{cm}^{-1}$  for CSO, 1465.17  $\text{cm}^{-1}$  for GNO and 1455.88  $\text{cm}^{-1}$  for PKO); C-O, C-C stretching vibration of alkoxy esters for (1164.88  $\text{cm}^{-1}$  for CSO, 1162.71  $\text{cm}^{-1}$  for GNO and 1160.19  $\text{cm}^{-1}$  for PKO); bending of alkenes and overlapping of rocking vibration of methylene (723.77  $\text{cm}^{-1}$  for CSO, 722.29  $\text{cm}^{-1}$  for GNO and 721.75  $\text{cm}^{-1}$  for PKO). The shoulders at 1652.01  $\text{cm}^{-1}$  for CSO, 1652.71  $\text{cm}^{-1}$  for GNO and 1644.83  $\text{cm}^{-1}$  for PKO are for C=C stretching vibration, one of the two distinct absorption bands typically observed

in oils containing unsaturated fatty acids (Yusuf *et al.*, 2015).

Other characteristics peaks observed are peculiar to GNO and PKO and another to only GNO. These peaks are used to monitor the degree of unsaturation in oils. The peak at 1417.73  $\text{cm}^{-1}$  for GNO and 1417.10  $\text{cm}^{-1}$  for PKO are ascribed to bending and rocking vibration of C-H of methyl or  $\text{CH}_3$  and 3007.65  $\text{cm}^{-1}$  for GNO is ascribed to =CH asymmetrical stretching vibration of double bond of alkenes. The peak at 1236.87  $\text{cm}^{-1}$  for GNO corresponds to stretching vibration of C-O alkoxy esters, ethers and C-O and peaks at 2854.25  $\text{cm}^{-1}$  for CSO, 2853.80  $\text{cm}^{-1}$  for GNO and 2853.36  $\text{cm}^{-1}$  for PKO correspond to symmetrical stretching vibration of C-H (methylene).

The infrared spectra of the biodiesels synthesized from castor, palm kernel and groundnut oils are shown in Figure 2, 4, 6. In a typical FT-IR spectrum of biodiesel from vegetable oils, the characteristic peaks found include the strongest peaks at 1740-1750  $\text{cm}^{-1}$  (the C=O vibration), the C-O esoteric vibrations of approximately 1170-1200  $\text{cm}^{-1}$  and a signal at <1500  $\text{cm}^{-1}$ , which is the methyl ester (O- $\text{CH}_3$ ) with its deformation vibration (Saifuddin and Refal, 2014). The peaks observed for these biodiesel produced from these three oils also showed similar bands and most of the bands correspond to that reported by Oyerinde and Bello (2016) and Saifuddin and Refal (2014). The major band (1740-1750  $\text{cm}^{-1}$ ) for biodiesel were observed for the three oils with very sharp peaks and this is ascribed to C=O (ester carbonyl functional group in FAPE). This group indicates the conversion of triglycerides in the oil to propyl ester. The peaks that indicate the double bond around 3000  $\text{cm}^{-1}$  and 725  $\text{cm}^{-1}$  are prominent in the three spectra. The band at approximately 3000  $\text{cm}^{-1}$  (HC=CH stretching) and 725  $\text{cm}^{-1}$  (out of plane bending show a slight decrease in the intensity for PKO and GNO, indicating decrease in saturation. This may be due to high percentage of saturated fatty acids in PKO and GNO which caused the oil to have higher stability as compare with CSO. As

discussed before, this band ( $3000\text{ cm}^{-1}$ ) corresponds to the cis double bonds present (Saifuddin and Refal, 2014). The GNO showed better sharp peaks compare with CSO and PKO at  $1000\text{-}1500\text{ cm}^{-1}$  which indicates the stretching vibration of C-O alkoxy esters, ether and C-O and also bending and rocking vibration of C-H (methyl or  $\text{CH}_3$ ).

The region  $678\text{-}960\text{ cm}^{-1}$  indicate the presence of = C-H functional groups. Though, this is more spelt out in GNO than PKO and CSO. They possess bending type of vibrations appearing at low energy and frequency region in the spectrum and they are all double bonded. They are attributed to Olefinic (alkenes) functional groups

in the biodiesel and they are unsaturated. They are part of the fatty acid propyl esters with unsaturated bond in the biodiesel, such as propyl oleate and propyl linoleate. The specific peak around  $750\text{ cm}^{-1}$  which was observed for the three oils but with sharp peak in GNO spectrum was overlapping by =C-H group which has the rocking mode of vibrations. This group indicates methylene functional group in the biodiesel ( $-(\text{CH}_2)-$ ). The rocking mode of vibration further helps to know more about the basic structure of FAPE component in the biodiesel and it is an indication that the biodiesel consist of long chain aliphatic structure (Oyerinde and Bello, 2016).

**Table 6: Functional group frequencies of CSO, GNO, PKO and biodiesels identified**

Wavenumber ( $\text{cm}^{-1}$ )			Types of vibration	Functional group
CSO	GNO	PKO		
3445.51	3466.43	3459.87	Stretching	O-H (alcohol)
	3007.65		asymmetrical stretching	=C-H(alkanes)
2925.73	2924.89	2924.03	asymmetrical stretching	C-H(alkanes)
2854.25	2853.80	2853.36	asymmetrical stretching	C-H(methylene)
1746.70	1744.95	1746.67	Stretching	C=O(triglyceride ester linkage)
1740-1750			Stretching	C=O(ester carbonyl functional group in FAPE)
1652.01	1652.71	1644.83	Stretching	C=C
1456.02	1465.17	1455.88	Bending	$\text{CH}_3$ (twisting)
	1417.73	1417.10	rocking of cis-disubstituted	CH(methyl)
	1236.87		stretching	C-O alkoxy esters, ethers & C-O
1164.88	1162.71	1160.19	out-of-plane bending	C-H( <i>cis</i> distributed olefins)
723.77	722.29	721.75	Overlapping rocking and out-of-plane bending vibration of methylene and alkene	=C-H and $-(\text{CH}_2)_n$ methylene groups ( <i>cis</i> distributed alkenes and olefins)

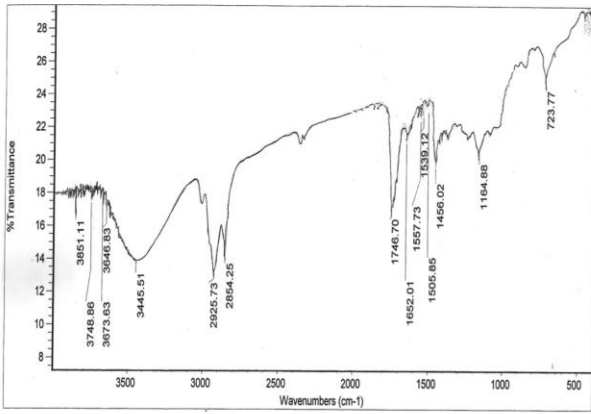


Fig 1: FT-IR Spectrum for CSO

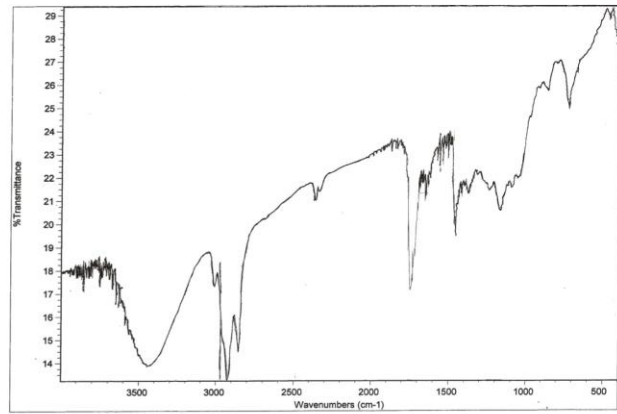


Fig 2: FT-IR Spectrum of Biodiesel Produced from CSO

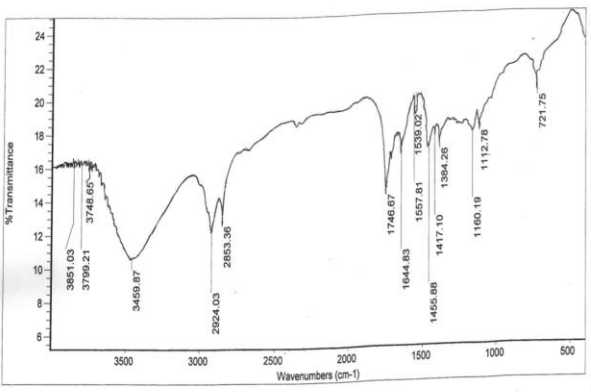


Fig 3: FT-IR Spectrum for PKO

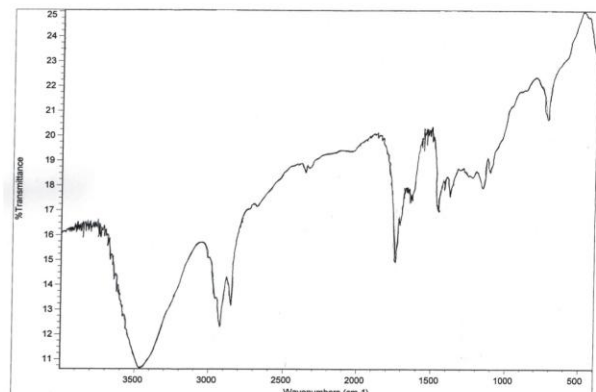


Fig 4: FT-IR Spectrum of Biodiesel Produced from PKO

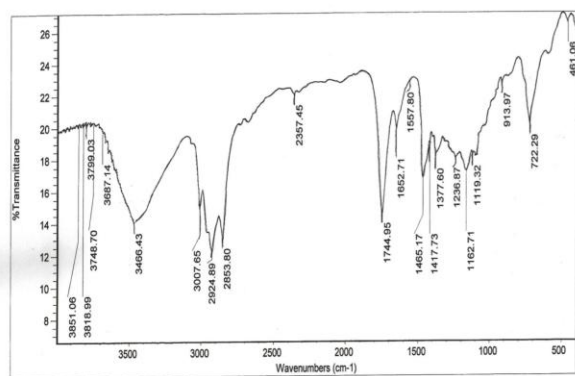


Fig 5: FT-IR Spectrum for GNO

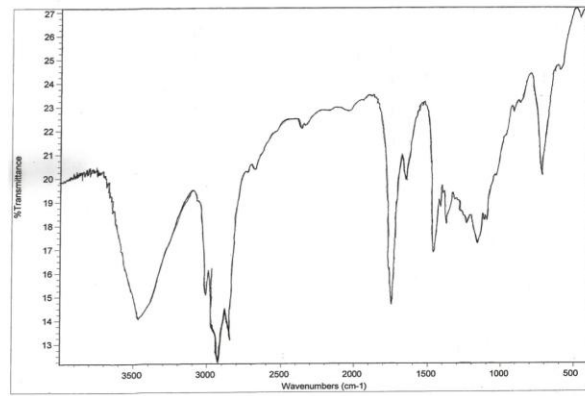


Fig 6: FT-IR Spectrum of Biodiesel Produced from GNO

## CONCLUSIONS

The potentials of biodiesel identified as an economical, clean-burning and sustainable source of fuel, now and for the future cannot be underrated. This has led to a growing global commitment to their use. Biodiesels has been produced from vegetable oils through alkali-catalyzed transesterification process.

The chemical analysis of the biodiesels produced showed good fuel properties and the infrared (IR) analysis of the biodiesels showed primary absorption bands that give fundamental knowledge of the type of the chemical group present in the biodiesels.

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