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## Production of Biodiesel From Peanut Oil Catalysed by Modified Clay

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**ABSTRACT**

Biodiesel production via heterogeneous esterification of peanut oil extracted from peanut was carried out using clay minerals which are believed to have promising future in catalytic properties. The clay samples were calcined (400 °C) and modified with H<sub>2</sub>SO<sub>4</sub> (50%) and NaOH (25%). The calcined and modified clay samples were characterised using FTIR and XRD. Transesterification conditions were; oil to methanol ratio of 1:9, reaction time and temperature, 2 h and 65 °C respectively while the catalyst dosages were 5%, 9% and 15%. The highest conversion observed was 72.24% for the 5% acid modified while the lowest was 19.85% for the 5% alkali modified clay. The presence of silica is confirmed from the absorption peaks at 1028 cm<sup>-1</sup>. FTIR peak at 823.23 cm<sup>-1</sup> corresponds to Si-O stretching vibration as well as the presence of Al-O bonds. Also, a band at 660 cm<sup>-1</sup> in the unmodified clay confirms the presence of Si-O-Si and Si-O-Al bonds respectively. These are typical frequencies for clay samples. The clay samples were also very crystalline as demonstrated by the distinct diffraction patterns of the XRD. These are believed to be good sites for catalytic activities. Important fuel properties of the methyl esters produced from the transesterification process compared well with ASTM D 6751-10 standards. This implies that environmentally benign materials such as clay minerals, which are abundant in availability are good alternatives of the other traditional catalysts employed in this process. These clay materials can thus be harnessed for commercialisation.

**Keywords:** Transesterification, Catalyst dosage, peanut oil, modified clay, Biodiesel

**INTRODUCTION**

Biodiesel production is of global interest and has gained worldwide attention in the last decade due to its environmental benefits biodegradability, low toxicity, low emission profile and renewability (Ayten *et al.*, 2011; Oniya *et al.*, 2014; Talha *et al.*, 2016). It is classified as a renewable resource because, it can be produced from natural sources that can easily be replenished after every use without any form of depletion.

Biomass is the major origin from where biodiesel can be synthesised. A major advantage of biodiesel therefore is its high flash point (100 °C minimum) as well as the fact that it does not emit any form of gaseous oxides e.g. sulphur oxides (SO<sub>2</sub> and SO<sub>3</sub>), nitrogen oxides (NO and NO<sub>2</sub>) hence it is environmentally benign (Oniya *et al.*, 2014). Biodiesel also releases minimum amount of carbon oxides, (CO and CO<sub>2</sub>), when combusted.

These are the major causes of the depletion of the ozone layer, which causes global warming. Therefore, the use of biodiesel can lead to significant reduction of CO<sub>2</sub> emission from 65 - 90% less, compared to the use of conventional fossil diesel (Ayten *et al.*, 2011; Oniya *et al.*, 2014; Talha *et al.*, 2016; Sharma, 2009). It can therefore be recognised as 'green fuel' (Sharma, 2009; Yusuff *et al.*, 2017). The term biodiesel refers to the alkyl monoesters of fatty acids produced from a renewable feedstock such as vegetable oils or animal fat and an alcohol. Glycerine is the primary by-product of the reaction (Ayten *et al.*, 2011; Talha *et al.*, 2016). It typically involves the transesterification of a triglyceride with methanol or other short-chain alcohols to produce fatty acid methyl ester (FAME) (How, 2013; Okoronkwo *et al.*, 2012; Pandiagan *et al.*, 2017; Romano *et al.*, 2011). Through this process, the high viscosity of vegetable oil is reduced to a value closer to that of diesel (Ayten *et al.*, 2011; Romano *et al.*, 2011; Igbum *et al.*, 2013).

Biodiesel as an alternative fuel can be used in its pure form or can be co-fired with petroleum diesel for use in compression diesel engines. Biodiesel blends with diesel fuels are indicated as "BX", where "X" is the percentage of biodiesel in the blend. For example, "B10" means a blend with 10% biodiesel and 90% diesel fuel and "B50" indicates an equal mixture of biodiesel and fossil fuel diesel; in consequence however, B100 indicates pure biodiesel (Ayten *et al.*, 2011; Yusuff *et al.*, 2017;

Romano *et al.*, 2011; Igbum *et al.*, 2013; Bello and Agge, 2012). The drawbacks of biodiesel however include higher freezing point than diesel fuel, meaning that it may not be conveniently used in cold climates. It is less stable than diesel fuel, implying that long term storage for more than six months is not recommended, higher cost when compared to diesel obtained from petroleum as well as degradation of plastic and natural rubber gaskets and hoses when used in pure form (Romano *et al.*, 2011; Igbum *et al.*, 2013; Bello and Agge, 2012; Shriyash, 2016). The American Standards for Testing and Materials (ASTM) is the regulatory body responsible for setting standards for biodiesel production under code 6751 (Ayten *et al.*, 2011; Oniya *et al.*, 2014; Talha *et al.*, 2016; Romano *et al.*, 2011; Igbum *et al.*, 2013; Bello and Agge, 2012; Shriyash, 2016).

The capability of producing biodiesel from different raw agriculture materials such as edible and non-edible oils is increasing globally (Abdul *et al.*, 2017; Soetaredjo *et al.*, 2011; Prafulla *et al.*, 2009; Ranga, 2017) and with the growing human population, many alternatives have been employed. Among the aforementioned oil resources however, peanut is chosen in this research to investigate the kinetics of transesterification for conversion into biodiesel (methyl/ethyl ester). Vegetable oils and/or animal fat can be converted to fuel for diesel engines through four major possible ways: direct use or blending of oils, micro-emulsion, thermal cracking or pyrolysis and transesterification reaction (Ayten *et al.*, 2011; How, 2013; Okoronkwo *et al.*, 2012).

Among all these methods however, the most preferred one is transesterification reaction, this is because transesterification reactions enable the use of diverse feedstock types to produce a fuel that highly resembles the conventional fossil fuel diesel in quality. This method converts oils and

fats (triglycerides) to their alkyl esters with viscosity similar to diesel fuel (Talha *et al.*, 2016; Yusuff *et al.*, 2017; Pandiagan *et al.*, 2017; Romano *et al.*, 2011). Transesterification is therefore defined as the reaction of a fat or oil with alcohol in the presence of a catalyst to form esters and glycerol. It is a direct conversion of one ester to another through interchange of special functional groups called alkoxy moiety. The by-product of the reaction is glycerine; it has commercial value (Talha *et al.*, 2016; Yusuff *et al.*, 2017) and several other uses. The general transesterification reaction is given below



Transesterification reaction can either be catalysed or non-catalysed, base or acid catalysed or enzyme catalysed such as lipase-catalysed transesterification. There are also some less investigated ways to produce biodiesel through esterification of oils such as using Nano-catalyst and ionic liquid catalyst (Yusuff *et al.*, 2017; Okoronkwo *et al.*, 2012).

These catalysts can either be homogenous or heterogeneous catalyst (Yusuff *et al.*, 2017; Okoronkwo *et al.*, 2012; Romano *et al.*, 2011; Igbum *et al.*, 2013; Bello and Agge, 2012). Catalyst such as  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  are acid based homogenous catalyst while alkaline based homogenous catalyst includes  $\text{KOH}$  and  $\text{NaOH}$  (Yusuff *et al.*, 2017; Bello and Agge, 2012). Alkali homogeneous catalyst has several advantages such as simple operating conditions, high reactivity and shorter reaction time while acid homogeneous catalyst aids simultaneous esterification and transesterification, which is a major reason why it is most suitable for oils with high free fatty acid (FFA) content (Romano *et al.*, 2011).

The use of homogenous catalyst however has

limitations such as; it operates at high temperatures, it is difficult to recycle, it is also corrosive in nature as well as the fact that alkali homogenous catalyst can react with FFA to form undesirable substance such as soap which lowers the pH of fatty acid methyl esters (Yusuff *et al.*, 2017; How, 2013; Romano *et al.*, 2011). Heterogeneous catalysts on the other hand have the ability to give higher yield without causing much downstream problems (Talha *et al.*, 2016; Yusuff *et al.*, 2017; How, 2013). Other advantages of heterogeneous catalysts include; comparatively lower cost of production, highly sustainable as well as the ability to be easily separated and reused after the reaction. These features of heterogeneous catalyst are due to their existence in a different phase from the reactants or products. Examples of these catalysts include calcium oxide  $\text{CaO}$  and Iron sulfate,  $\text{Fe}_2\text{SO}_4$  (How, 2013; Okoronkwo *et al.*, 2012). Several types of heterogeneous catalyst have been developed and assessed; of particular interest is clay soil (Romano *et al.*, 2011). For this research however,  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  modified clay is used as the catalyst.

## MATERIALS AND METHODS

Peanut and clay samples were acquired from Wadata market, in Makurdi and Naka in Gwer West LGA respectively, all in Benue, Nigeria. The Clay samples were sundried for 5 days, pulverized then sieved with a  $2 \mu\text{m}$  micro sieve. Further drying was carried out for 4 h (Gbarakoro *et al.*, 2013), then samples then stored in an air tight sample container. Calcination was carried out in pre-treated crucibles at  $400^\circ\text{C}$  for 4 h.

### Modification of Clay

An amount (50 g) of the calcined clay was acid modified by mixing in  $\text{H}_2\text{SO}_4$  (50% wt/wt), the mixture was heated under reflux at  $90^\circ\text{C}$  for 3 h with continuous stirring. After this interval, the mixture was allowed to cool to room temperature

then filtered, washed severally in distilled water then placed in an oven at 100 °C overnight.

Another portion of the calcined clay (50 g) was transferred into a 250 mL heating flask. 8.25 mL of NaOH (25% wt/wt) was also measured into a beaker. Furthermore, distilled water was used to make up the alkali up to the 100 mL mark before being transferred into the heating flask containing the clay sample. It was then placed on the heating mantle to heat at 90 °C under reflux for 3 h with continuous stirring. The slurry formed after the impregnation was transferred into already pre-treated evaporating dishes and placed in an oven to dry to 100 °C for 24 h.

#### **Transesterification Reaction of peanut oil**

Biodiesel was produced from peanut oil with 1:9 oil to methanol molar ratio using (50% wt/wt) acid modified and (25% wt/wt) alkali modified clay respectively with 5%, 9% and 15% catalyst dosage at 65 °C for 2 h for all samples. The result was then filtered and transferred into separatory funnel for further reaction to occur overnight. Two (2) layers were formed after the completion of the reaction. The glycerine was decanted and the biodiesel was collected and stored.

#### **Extraction of Oil from Peanut**

Oil was extracted from the pulverised peanut using a Soxhlet tube at 65 °C for 6 h under reflux using hexane. The oil collected after the hexane was recovered was left to stand in an open beaker for the residual hexane to evaporate.

#### **Determination of percentage yield of peanut oil and peanut biodiesel**

The percentage yield was determined after evaporating the residual hexane and the percentage yield was calculated from the relation:

% yield = weight of the sample / weight of the sample before use x 100

#### **Determination of Density of Peanut Oil and Peanut Biodiesel**

The density of the sample was carried out using a 50 mL density bottle. The density bottle was properly washed, dried, weighed and filled with water to the mark and weighed. The bottle was emptied, dried and filled with the sample and weighed. The density was calculated using the relation:

$$\text{Density } \rho = \frac{w - m}{\text{volume of the density bottle}}$$

Where m = weight of empty density bottle

w = weight of empty density bottle + weight of sample

#### **Determination of colour of Peanut Oil and Peanut Biodiesel**

The colour of the peanut oil and POB was determined by visual observation

#### **Determination of Specific Gravity of Peanut Oil and Peanut Biodiesel**

The specific gravity of the sample was determined from the ratio of the density of the sample to the density of the water at room temperature. The relationship is given as:

$$\text{Specific gravity} = \frac{\text{density of sample}}{\text{density of water}}$$

#### **Determination of Refractive Index and viscosity of Peanut Oil and Peanut Biodiesel**

A drop of the sample was introduced onto the lens of the Refractometer, temperature of the system was 30 °C and through the binocular lenses, the dark portion was viewed and adjusted to be in line with intersection of the cross and the refractive index was taken from the pointer against the internal monochromatic source of light found on the device. For the viscosity, a digital Brookfield Viscometer (model DV-II+Pro) was used to determine the viscosity of the oil extracted. A

certain amount of the oil was introduced into a sample holder and a standard spindle was immersed into it and readings were taken accordingly

#### Determination of Kinematics Viscosity of Peanut Oil and Peanut Biodiesel

The kinematics viscosity was calculated from the relation:

$$\text{Kinematics Viscosity} = \frac{\text{dynamic viscosity}}{\text{density of sample}}$$

#### Determination of Saponification Value of Peanut Oil and Peanut Biodiesel

A 2.0 g weight oil sample was weighed into a 250 mL heating flask. A 25 mL of 0.5 N KOH was added to the sample in the flask. The mixture was then placed on a heating mantle to heat under reflux for 30 min with constant shaking. Afterwards, 1 mL of phenolphthalein solution was added and the mixture was titrated while hot with 0.5 M hydrochloric acid. The initial and final titre value was recorded accordingly. A blank reaction was also carried out that is, repeating the above procedure without the sample. The saponification value was calculated using the following formula:

$$\text{Sap value} = \frac{56.1 (B - S) \times N \text{ of HCl}}{\text{Wt of sample}}$$

#### Determination of Acid Value and Free Fatty Acid Value of Peanut Oil and POB

A 250 mL heating flask was washed and placed in an oven to dry. Sample (2 g) was then weighed into the flask. Furthermore, 50 mL of neutralised 1:1 (v:v) ethanol and diethyl ether solution was also measured and poured into the flask containing the sample. It was then placed on a heating mantle to heat for 10 min; this is to ensure proper mixing of the mixtures.

Afterwards, 1 mL of phenolphthalein was added and shaken vigorously to homogenize the mixture. It was then allowed to cool and titrated with 0.5 M KOH solution. A blank reaction was also carried out

without the sample. The acid value is calculated from the expression:

$$\text{Acid value} = \frac{56.1 (B - S) \times N \text{ of KOH}}{\text{Wt of sample}}$$

$$\text{Free fatty acid (\%)} = \frac{\text{acid value}}{1.99}$$

#### Procedure for FTIR Analysis of the Clay Samples

The powdered sample catalysts were pressed into thin self-supporting wafer discs 1.6 cm diameter with the aid of a SPECEC hydraulic press. These discs typically weighed < 30 mg. These sample discs were pre-treated under different conditions as required for the particular experiment under investigation but were typically pre-treated under low vacuum ( $10^{-3}$  mbar) and then high vacuum ( $10^{-6}$  mbar). These were subsequently activated in a CaF<sub>2</sub> material IR cell with thermal treatment and optical sections under the chosen conditions. The experimental set-up was such that it contained a furnace where the sample catalyst discs could be pre-treated under desired temperature conditions before lowering them for the IR measurements. Measurements were thus carried out at room temperature after the various pre-treatments. The FTIR spectra were measured over a range of 3000 - 1000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and 150 scans for signal accumulation for all measurements.

#### Procedure for X-ray Diffraction Analysis of Clay Samples

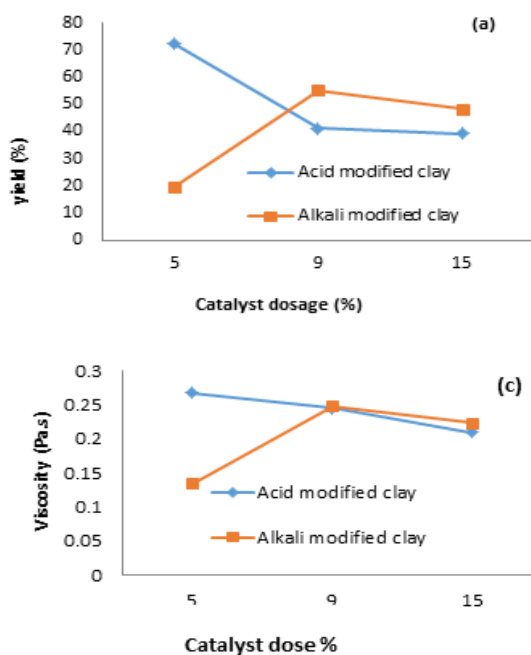
Clay samples were pelletised and sieved to 0.074 mm. These were later taken in an aluminum alloy grid (35 mm x 50 mm) on a flat glass plate and covered with a paper. Each sample was run through the Rigaku D/Max-III C X-ray diffractometer developed by the Rigaku Int. Corp. Tokyo, Japan and set to produce diffractions at

scanning rate of 2 °/min in the 2 - 50 °/min at room temperature with a CuK $\alpha$  radiation set at 40 kV and 20 mA. The diffraction data (value and relative intensity) obtained was compared to that of the standard data of minerals from the mineral powder diffraction file, ICDD which contained and includes the standard data of more than 3000 minerals. Similar diffraction data means the same minerals to standard minerals which exist in the soil sample.

## RESULTS AND DISCUSSION

**Table 1:** Physicochemical Properties of Peanut Oil

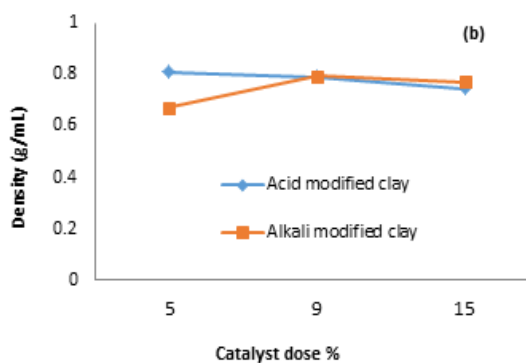
S/No	Parameter	Value
1.	Yield (%)	46.3
3.	Density at 30 °C (g/mL)	0.8868
4.	Specific gravity at 30 °C	0.8947
5.	Refractive index	1.465
6.	Kinematic viscosity at 29 °C (cm <sup>2</sup> /s)	0.35
7.	Viscosity at 29 °C (Pa.s)	0.031
8.	Saponification value (mg KOH/g)	200.56
9.	Acid value (mg KOH/g)	4.01
10.	Free fatty Acid (%)	2.02
11.	Colour	Pale yellow



### .FTIR of Clay Catalysts

The FTIR spectra for unmodified clay as well as acid modified and alkali modified clay displayed similar characteristic peaks, a broad absorption band at the wavenumber of 3483 cm<sup>-1</sup> is a characteristic vibration band associated with stretching of O-H functional group, indicating the presence of bonded O-H group or adsorbed water molecules in the sample. The presence of absorbed water molecules is supported by the absorption band located at 1628.80 cm<sup>-1</sup>, commonly assigned to bending vibration of absorbed water molecule.

The presence of silica is confirmed from the absorption peaks at 1028 cm<sup>-1</sup>. The peak at 823.23 cm<sup>-1</sup> also corresponds to Si-O stretching vibration as well as the presence of Al-O bonds. The band at 660 cm<sup>-1</sup> in the unmodified clay confirms the presence of Si-O-Si and Si-O-Al bonds respectively.



**Figure 1:** Effect of catalyst dosage on the (a) yield (b) density and (c) viscosity of biodiesel at molar ratio of 1:9, 2 h, and 65 °C

**Table 2: Physicochemical Properties of Peanut Oil biodiesel**

Parameters	Peanut Oil	Peanut oil Biodiesel						ASTM D6751-10 (Ogemdi & Ibraheem, 2018)
		Acid modified (H <sub>2</sub> SO <sub>4</sub> ) catalyst			Alkali modified (NaOH) catalyst			
Catalyst dosage (%)	-	5	9	15	5	9	15	-
Oil/methanol ratio	-	1:9	1:9	1:9	1:9	1:9	1:9	-
Yield (%)	46.3	72.24	41.05	39.16	19.85	55.18	48.41	-
Density @ 30 °C(g/mL)	0.887	0.811	0.789	0.745	0.671	0.795	0.772	-
Sp. Gravity @ 30 °C	0.895	0.823	0.802	0.774	0.684	0.801	0.724	0.87-0.90
Refractive index	1.465	1.465	1.467	1.469	1.466	1.468	1.469	1.4665
Kinematic viscosity (cm <sup>2</sup> /s)	0.350	0.330	0.311	0.282	0.201	0.312	0.290	1.9-0.6
Absolute viscosity (Pa.s)	0.310	0.268	0.245	0.210	0.135	0.248	0.224	-
Sap. Value (mg KOH/g)	200.56	256.66	-	-	-	260.47	-	-
Acid value (mg KOH/g)	4.01	1.40	-	-	-	1.10	-	0.8 max
FFA (%)	2.02	0.70	-	-	-	0.55	-	-
Colour	Pale yellow	Pale yellow	Yellow	Yellow	Light yellow	Pale yellow	Pale yellow	-

**Table 3: FTIR values for unmodified and modified clay**

Functional group	Wave number (cm <sup>-1</sup> )		
	Unmodified clay	H <sub>2</sub> SO <sub>4</sub> modified clay	NaOH modified clay
OH stretching	3500-3730.40	3200-3737.60	3400-3725.60
Si-O bond	1028.00	1031.20	1033.60
Si-O stretching	823.23	795.20	854.40
Al-O bond	823.23	795.20	854.40
Si-O-Si bond	660.80	683.20	696.80
Si-O-Al bond	660.80	683.20	696.80
CO <sub>3</sub> <sup>2-</sup>	1389.60	1387.20	1391.20

More so, the band at 1389.60 cm<sup>-1</sup> depicts the presence of CO<sub>3</sub><sup>2-</sup>, indicating the probability of the formation of potassium carbonates. With respect to the existence of functional groups Si, O, and Al are all observed in the spectrum. From the FTIR spectrum in **figure 2b**, it was observed however that most of the bands were shifted to the lower wavenumber after the clay was modified with an acid and higher wave number after the clay was modified with an Alkali as seen in **figure 2c**.

### The X- Ray Diffraction Analysis of the Modified Clay Samples

The diffracted patterns of the acid modified clay showed patterns of muscovite at 35°, kaolinite between 20-24° and 60-63° respectively, illites at 47°, dolomites at 45° and 55°, quartz at 11°, 20°, 25°, 38° and 41° respectively, microcline at 69° and calcite at cite at 51°. The alkaline modified clay showed patterns of mica at slightly above 55° and

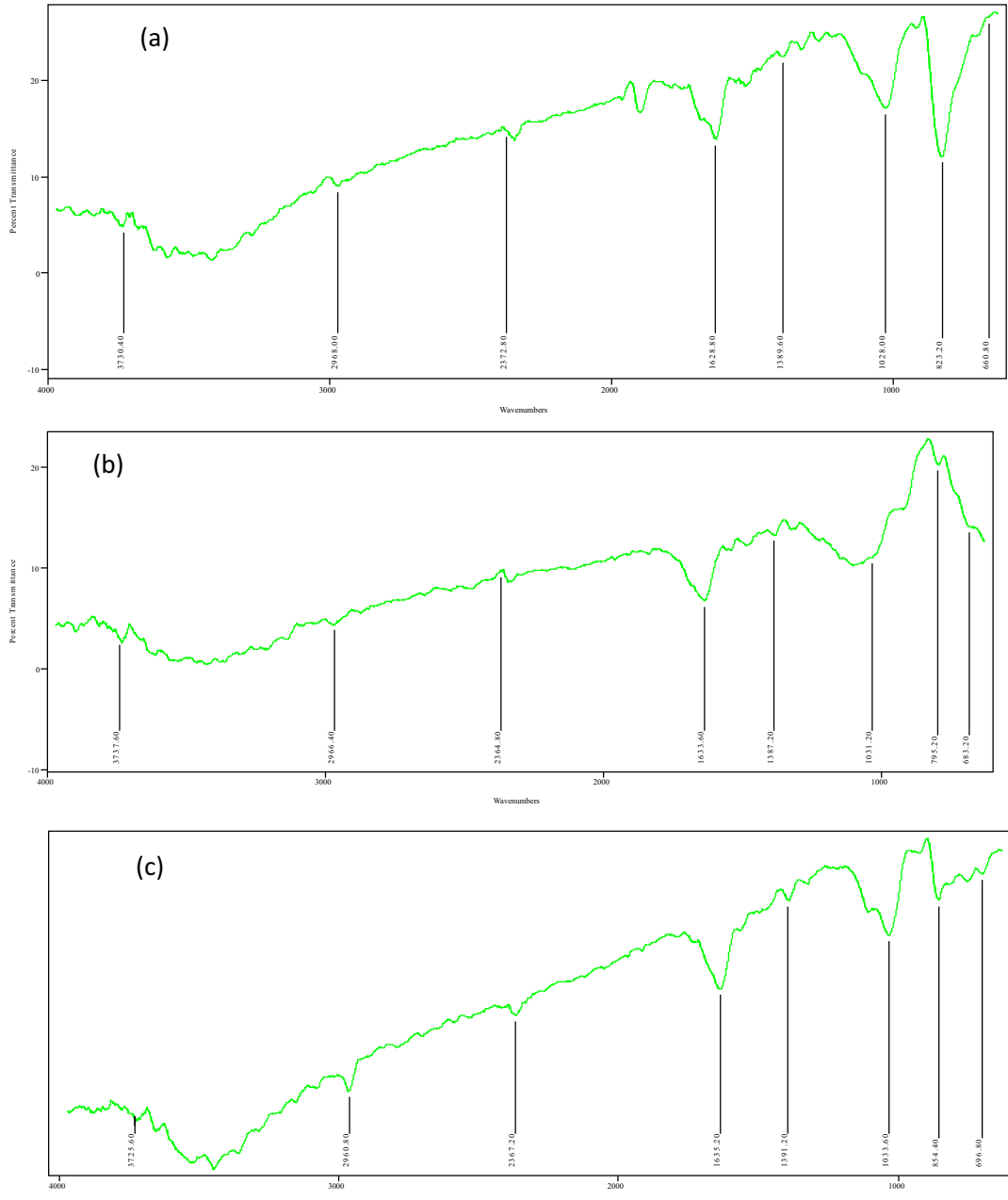


Figure 2: FTIR spectrum of (a) unmodified (b) acid modified (c) alkali modified Clay



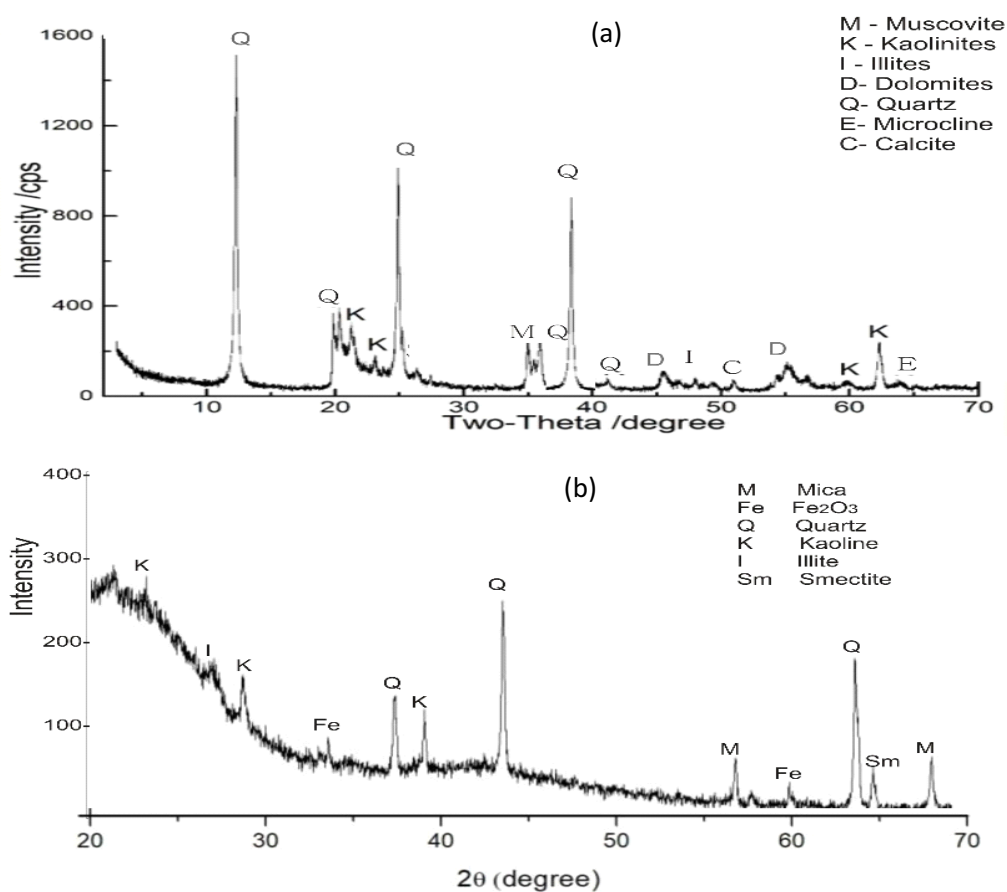


Figure 3: The XRD result of the (a) acid modified and (b) alkali modified clay

close to 70°, patterns of iron oxide were seen at 33° and 60° respectively, patterns of quartz were seen between 35-40°, 44°, and 64°, kaolinite were seen at 23° and about 39°, illite was seen at about 37° and smectite was seen at 65°. It is observed that muscovite, dolomites, microcline and calcite were present in the acid modified clay but were absent in the alkaline modified clay. Whereas, mica, iron oxide, and smectite were found in the alkaline modified clay but were not found in the acid modified clay. This could be as a result of the variation in the reaction of acid and alkali with the clay samples. It can be seen from the patterns of the

X-ray diffractions that the acid modified clay have more distinct peaks than the alkaline modified clay. The crystallinity of the clay and the presence of minerals is responsible for its absorption property and hence catalytic activity on biodiesel production

### Nature of peanut oil produced

#### i. Yield

The mass of peanut used for the extraction was 326.66 g and it yielded 134.47 g of peanut oil, corresponding to a 46.3% oil yield. 166.32 g of peanut chaff was recovered after the reaction.

### I. Density, Specific gravity and Refractive Index

Results of the density of peanut oil at ambient temperature was 0.8868 g/ml (Table 1). The specific gravity of peanut oil at the same temperature was also observed to be 0.8947 g/ml. More so, the kinematic viscosity of the peanut oil was  $0.35\text{cm}^2/\text{s}$  while its absolute viscosity was 0.031 Pa.s. These values for density and viscosity show that, the peanut oil is too viscous and highly dense and thus not suitable to be used directly in diesel engines, transesterification process is therefore employed to reduce the density and viscosity. Transesterification shortens the chain length which by implication causes a reduction in density and viscosity. The refractive index of peanut oil was determined to be 1.465, which makes it suitable to be used for biodiesel production.

### ii. Saponification value (SV)

The saponification value of peanut oil was found to be 200.56 mg KOH/g (Table 1) indicating a high percentage of fatty acids of low molecular weight and carbon chain length. This implies that the oil may have the potential for use in soap making or cosmetic production (Akanni *et al.*, 2005) and can also be suitable for production of biodiesel. Saponification value has been reported to be inversely related to the average molecular weight of the fatty acids in the oil fractions (Odoom and Edusei, 2015). Oil fractions with saponification values  $\geq 200\text{mgKOH/g}$  has been reported to possess low molecular weight fatty acids (Odoom and Edusei, 2015; Afolabi, 2008).

### iii. Acidity

The free fatty acid content of oils denotes the quality and edibility of oil. A previous research has shown that, the Polish Directive from the minister of health from 25 September, 2012, showed that the acceptable level of free fatty acids in frying medium cannot exceed 2.5 mg KOH/g of fat (Aniolowska *et al.*, 2016). This implies that oils with high free fatty acid are not suitable for consumption but for other

uses such as production of biodiesel. As shown in Table 1, the acid value of the extracted peanut oil however was 4.01 mg KOH/g which indicates that the oil is more suitable for biodiesel production and might need to undergo further purification if it is to be edible. The peanut oil also contains 2.02% free fatty acids (FFA). These FFAs are prone to oxidation which can cause rancidity of the oil and their content in oil samples also influences biodiesel yield and purity as well their shelf life.

### Nature of Biodiesel produced

#### i. Yield

In this work, the molar ratio of oil to methanol (1:9), reaction temperature ( $65\text{ }^\circ\text{C}$ ) and reaction time (2 h) were kept constant throughout the reaction; the catalyst dosage was however varied which results to different biodiesel yields obtained.

As shown in Figure 1 the two (2) modified clay samples were used as catalyst for the in 5%, 9%, and 15% catalyst dosage proportions in each case. It was observed that the reaction catalysed with acid modified clay, 5% catalyst dosage gave the highest yield of 72.24% which is much higher than the 41.05% gotten from 9% catalyst dosage and 39.96% gotten from 15% catalyst used for the reaction. By implication, increasing the dosage of catalyst reduces the yield of biodiesel.

Furthermore, for the reaction catalysed with Alkali modified clay at constant oil to methanol ratio and varying only the catalyst dosage, it was observed that 9% catalyst dosage gave the highest yield of 55.0% as against 48.4% for 15% catalyst dosage and 19.9% for 5% catalyst dosage. This implies that lower catalyst dosage gives a lower biodiesel yield and increasing the dosage increases its yield till it gets to a threshold point (9%) where increasing the catalyst dosage results in a decrease in yield.

### ii. Density and Specific gravity

One of the aims of transesterification is to reduce the density and viscosity of oils. Density of peanut biodiesel also reduces with increasing catalyst dosages for products obtained from the reaction catalysed by acid modified clay. The density increases for the products catalysed by Alkali modified clay as shown in Figure 1. Generally, the values obtained for densities of the biodiesels produced were for both acid and alkali were significantly lower than that for the source oil. This infers that transesterification occurred. The values of specific gravities of all the biodiesel at their viscosities mentioned ranged from 0.684–0.823 g/ml for all the catalyst dosages used. Even though, these values were slightly below the ASTM specification, there was a significant decrease from the value of the source oil, showing that transesterification took place.

### iii. Viscosity

Viscosity is the resistance to the flow of a liquid and is an important characteristic of a fuel which signifies the flow ability of the fuel. so it plays a good role in the spray atomization of the fuel. The biodiesel produced shows a significant decrease in the viscosity from the source oil. The viscosity decreases with increase in catalyst dosage for the acid modified clay as seen in Figure 1. However, the viscosity of the product from the alkaline modified clay is low at 5 % catalyst dosage and increases with 9 % catalyst dosage but further on, decreases with 15 % catalyst dosage. This inconsistency might be as a result of impurities associated with the production process.

### iv. Refractive index (RI)

The refractive index of biodiesel produced from peanut oil shows values that range from 1.465-1.469 at room temperature (Table 2). However, it was observed that an increase of catalyst dosage resulted in an increase in Refractive Index for both products obtained from the reaction catalysed by

both acid and Alkali modified clay. This values are almost the same with the ASTM specification for biodiesel.

### v. Saponification value

The Saponification value of the product of the reaction catalysed by alkaline modified clay is seen to be 260.471 mg KOH/g which is higher than that of the product of the reaction catalysed by acid modified clay 256.660 mg KOH/g as indicated in the results (Table 2). These values show a significant increase in the Saponification value of the peanut oil used for the reaction. The high Saponification value observed in the biodiesel indicates the shortening of the fatty acid bond length as a result of transesterification reaction. This has a direct implication on the reduction of the density and viscosity of the peanut oil after the reaction is complete. The higher the saponification value, the lower the fatty acid chain length and the lighter the mean molecular weight of the triglycerides

### vi. Acidity

As indicated (Table 2) the acid value of the product of the reaction catalysed by acid modified clay which is 1.40 mg KOH/g is higher than that of the product catalysed by the alkali modified clay 1.10 mg KOH/g. This shows a reduction in the acid value of the original peanut oil used for the reaction (4.01 mg KOH/g). The shortening of the fatty acid chain length during the reaction can be ascribed to the reduction of the acid value (from 4.01 mg KOH/g for peanut oil). Furthermore, it was also observed that the FFAs content (0.70%) of the product of the reaction catalysed by acid modified clay as well as that of the product of the reaction catalysed by an alkali modified clay (0.55%) shows a significant reduction from the value obtained from the original peanut oil used (2.02%) after the reaction. The lower percentage of free fatty acids in the biodiesel indicates that the biodiesel can be

stored for a longer time without going rancid. Even though this values were slightly above the ASTM specification for biodiesel, a significant deviation was seen from the value of the source oil implying that transesterification reaction took place.

### Characterisation of Clay by Fourier Transform Infrared Analysis (FTIR)

The FTIR spectra for unmodified clay as well as acid modified and alkali modified clay displayed similar characteristic peaks, a broad absorption band at the wavenumber of  $3483\text{ cm}^{-1}$  is a characteristic vibration band associated with stretching of O-H functional group, indicating the presence of bonded O-H group or adsorbed water molecules in the sample (**Figure 2**). The presence of absorbed water molecules is supported by the absorption band located at  $1628.80\text{ cm}^{-1}$ , commonly assigned to bending vibration of absorbed water molecule.

The presence of silica is confirmed from the absorption peaks at  $1028\text{ cm}^{-1}$ . The peak at  $823.23\text{ cm}^{-1}$  also corresponds to Si-O stretching vibration as well as the presence of Al-O bonds. The band at  $660\text{ cm}^{-1}$  in the unmodified clay confirms the presence of Si-O-Si and Si-O-Al bonds respectively (Soetaredjo *et al.*, 2011). Since clay is a sandy material, made up of silicon and aluminum compounds, these vibration bands confirm the presence of these compounds which are also reported to enhance the catalytic properties of the clay materials (Gbarakoro *et al.*, 2013).

More so, the band at  $1389.60\text{ cm}^{-1}$  depicts the presence of  $\text{CO}_3^{2-}$ , indicating the probability of the formation of potassium carbonates. With respect to the existence of functional groups Si, O, and Al are all observed in the spectrum (Pandiagan *et al.*, 2017; Abdul *et al.*, 2017). From the FTIR spectrum in Figure 2, it was observed however that most of the bands were shifted to the lower wavenumber after the clay was modified with an acid and higher wave

number after the clay was modified with an Alkali..

### CONCLUSION

Several solid catalysts have been investigated for biodiesel synthesis and their uses have been limited to reasons associated with their reaction rates, unfavorable side reactions and leaching problem. The current research has revealed the catalytic properties of clay minerals when used as catalyst for transesterification reaction as well as its behaviour when modified with an acid or alkali respectively. From the result, it can be seen that clay minerals can be a major source of low-cost catalyst in biodiesel production hence can be used as an alternative to synthetic catalyst which pose lots of drawbacks (Aigba *et al.*, 2021). Furthermore, after the properties of peanut oil were studied, they showed that the oil possesses most qualities suitable for use in the production of biodiesel which has similar properties to fossil diesel and can thus be considered an alternative source of fuel with higher environmental benefits (Aigba *et al.*, 2021; Stead *et al.*, 2019). The biodiesel produced from peanut oil substantially met the properties required of to be used as fuel according to ASTM standards.

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