# ECONSTOR

Make Your Publications Visible.

A Service of



Leibniz-Informationszentrum Wirtschaft Leibniz Information Centre for Economics

Folayan, Adewale Johnson; Anawe, Paul Apeye Lucky; Aladejare, Adeyemi Emman; Ayeni, Augustine Omoniyi

#### Article

Experimental investigation of the effect of fatty acids configuration, chain length, branching and degree of unsaturation on biodiesel fuel properties obtained from lauric oils, high-oleic and high-linoleic vegetable oil biomass

**Energy Reports** 

### **Provided in Cooperation with:**

Elsevier

*Suggested Citation:* Folayan, Adewale Johnson; Anawe, Paul Apeye Lucky; Aladejare, Adeyemi Emman; Ayeni, Augustine Omoniyi (2019) : Experimental investigation of the effect of fatty acids configuration, chain length, branching and degree of unsaturation on biodiesel fuel properties obtained from lauric oils, high-oleic and high-linoleic vegetable oil biomass, Energy Reports, ISSN 2352-4847, Elsevier, Amsterdam, Vol. 5, pp. 793-806, https://doi.org/10.1016/j.egyr.2019.06.013

This Version is available at: https://hdl.handle.net/10419/243628

#### Standard-Nutzungsbedingungen:

Die Dokumente auf EconStor dürfen zu eigenen wissenschaftlichen Zwecken und zum Privatgebrauch gespeichert und kopiert werden.

Sie dürfen die Dokumente nicht für öffentliche oder kommerzielle Zwecke vervielfältigen, öffentlich ausstellen, öffentlich zugänglich machen, vertreiben oder anderweitig nutzen.

Sofern die Verfasser die Dokumente unter Open-Content-Lizenzen (insbesondere CC-Lizenzen) zur Verfügung gestellt haben sollten, gelten abweichend von diesen Nutzungsbedingungen die in der dort genannten Lizenz gewährten Nutzungsrechte.



WWW.ECONSTOR.EU

https://creativecommons.org/licenses/by/4.0/

#### Terms of use:

Documents in EconStor may be saved and copied for your personal and scholarly purposes.

You are not to copy documents for public or commercial purposes, to exhibit the documents publicly, to make them publicly available on the internet, or to distribute or otherwise use the documents in public.

If the documents have been made available under an Open Content Licence (especially Creative Commons Licences), you may exercise further usage rights as specified in the indicated licence.



Contents lists available at ScienceDirect

## **Energy Reports**

journal homepage: www.elsevier.com/locate/egyr

Research paper

# Experimental investigation of the effect of fatty acids configuration, chain length, branching and degree of unsaturation on biodiesel fuel properties obtained from lauric oils, high-oleic and high-linoleic vegetable oil biomass

Adewale Johnson Folayan <sup>a,\*</sup>, Paul Apeye Lucky Anawe <sup>a</sup>, Adeyemi Emman Aladejare <sup>b</sup>, Augustine Omoniyi Ayeni <sup>c</sup>

<sup>a</sup> Petroleum Engineering, Covenant University, Nigeria, University of Ibadan, Nigeria

<sup>b</sup> University of Oulu, Pentti, Kaiteran Katu, Oulu, Finland

<sup>c</sup> Chemical Engineering Department, Covenant University, Nigeria

#### ARTICLE INFO

Article history: Received 16 March 2019 Received in revised form 31 May 2019 Accepted 23 June 2019 Available online xxxx

Keywords: Biomass Branching Chain length Cold flow behaviour Critical properties Gas chromatography Transesterification reaction Unsaturation

#### ABSTRACT

A very good understanding of the structure, level, type and physical property relationships of fatty acids in plants oils and their methyl esters (FAMEs) is of utmost importance when selecting vegetable oils for a particular desired biodiesel quality that meets the operating condition requirements of the compression-ignition diesel engine and the climatic dictate of the environment under which the engine is operated. It is on this premise that the degree of influence of fatty acid configuration, chain length, branching and unsaturation on cold flow and critical properties of biodiesel was investigated. The critical properties studied include: saponification and cetane number, iodine value, higher heating values, density, flash point and kinematic viscosity. The feed stock consists of three groups of vegetable oil biomass. The group one is made up of highly saturated, lauric coconut and palm kernel oils while group two consists of high linoleic, soyabean and corn oil biomass with low percentage of mono-unsaturated and high percentage of poly-unsaturated fatty acid. High oleic olive and canola oil constituted the third group of biomass. The triglycerides in these oils were converted to methyl esters by alkali-catalyzed transesterification reaction under standard conditions. The fatty acid methyl esters (FAMEs) compositional analyses of these feed stocks was done by using Agilent, HP 6890 Gas Chromatograph equipped with Flame ionization detector and 6890 Auto Sampler that connects with a controller box (GC-FID). The various biodiesel cold flow behaviour and critical properties under investigation were evaluated by the American society for testing materials (ASTM D6751-07b) and the European union (EN 14214) standard procedures and techniques.

Better cold flow behaviour was exhibited by biomass with higher degree of unsaturation, longer chain length, higher degree of branching and with cis configuration. While critical properties showed a lot of variations based on fatty acid profile.

© 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

#### 1. Introduction

The use of petroleum diesel in compression ignition engines have been tagged to have contributed significant percentage of various air pollutants such as oxides of nitrogen (NOx), carbon monoxide (CO), Carbon-dioxide (CO<sub>2</sub>), unburnt hydrocarbons (HCs) and soot as a result of incomplete combustion. The hazardous effect of these pollutants on both the environment and human health cannot be underestimated.

\* Corresponding author. E-mail address: folayanadewale03@yahoo.com (A.J. Folayan). Biodiesel is a clean burning fuel with low exhaust emissions, non-toxic, biodegradable fuel that is free from Sulphur, aromatic hydrocarbons, metal and crude oil residues that is used in compression ignition engines without any major modification. Hence, it has continued to be of interest in providing alternative energy source mainly because of its renewable nature (non-exhaustive), safe and its compatibility with existing direct injection engines.

However, biodiesel has substantially reduced emissions of unburnt hydrocarbons, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons and particulate matter (knothe et al., 1997; Van-gerpen et al., 2004a,b). Similarly, biodiesel helped to reduce green-house gas emission because

https://doi.org/10.1016/j.egyr.2019.06.013

2352-4847/© 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).







the net level of carbon-dioxide in the atmosphere is not increased by burning biofuels owing to the fact that Green House gases produced during the combustion of biofuels are recycled as carbon-dioxide during photosynthesis and absorption process by plant (Agarwal, 1998).

Various energy users began to search for alternatives to diesel and plants oil were seen as viable candidates without modifying their physico-chemical and fuel properties. The direct utilization of these unrefined oils became catastrophic on compressionignition engine because of their high iodine value, abnormally high kinematic viscosity, high cloud and pour points, excessively high density, high acid value leading to formation of carbon deposit, low cetane number and heating values (Bari et al., 2002).

These abnormal physical and chemical properties were sufficiently modified upon trans-esterification to conform to Both the American Standard for Testing Materials (ASTM) and the European standard (EN) requirements. Transesterification is the reaction of triglycerides in plants derived oil or fats with an alkanol (ethanol and methanol) in the presence of catalyst (acidic or alkaline) to form fatty acid alkyl ester (biodiesel) under optimum conditions.

According to Silitonga et al. (2011), Jatropha curcas is a nonedible feed stock for biodiesel production that does not bring about unhealthy competition with food. It offers immediate and sustained greenhouse gas advantages over other biofuels. Similarly, Silitonga et al. (2019) designed an experimental procedure for the optimization of transesterification reaction for biodiesel production by using Box-Behnken design. A methyl ester yield of 98.39% was obtained from transesterification of Reutealis trisperma oil. The optimum conditions for the reaction are methanol to oil molar ratio of 8:1, catalyst concentration of 1.2 wt%, temperature of 64 °C and reaction duration of 68 min. The optimum conditions for the conversion of triglycerides in native stone fruit oil to methyl ester with 95.8% yield according to Mohammed et al. (2018) are: methanol to oil molar ratio of 6:1, potassium hydroxide (KOH) catalyst concentration of 0.5 wt% and a reaction temperature of 55 °C. Also, biodiesel can also be produced from non-edible seed oils such as Hevea brasiliensis (HB) and Ricinus communis (RC) by esterification-neutralizationtransesterification reaction (ENT) process (Silitonga et al., 2016).

Vegetable oil consists of triglycerides extracted from plant with molecules of glycerol bounded to three fatty acid molecules. The structural features that affect the physical and chemical fuel characteristics of fatty acid methyl ester (FAME) are length of carbon chain, degree of saturation and branching of the chain. If the accurate knowledge of the influence of molecular structure of fatty acids in the plant oil and its composition is known, the various production parameters such as catalyst concentration and type, alcohol, reaction temperature and duration can be reliably selected for optimal transesterification process and good quality biodiesel production.

The most important difference between the chemical composition of fossil fuel (petro-diesel) and that of plant oils is the oxygen content. While vegetable oils contain between 10%–20% oxygen, fossil fuel has an insignificant amount of oxygen. This oxygen content in plant oils is responsible for higher brake specific fuel consumption in biodiesel (Anawe and Folayan, 2018a) because methyl esters have lower heating value compared to petroleum diesel. Oxygen has a lower heating value than hydrogen and carbon molecules.

#### 2. Materials and methods

#### 2.1. Saturated and unsaturated fatty acid

Fatty acids consist of a hydrocarbon chain that is bonded to a carboxyl group (COOH). Saturated fatty acids contain straight



Fig. 1a. Caproic acid (saturated).

chains of carbon atoms with only single bond and they conform to the general molecular formular CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>COOH. They include caproic acid ( $C_6$ ) (Fig. 1a), caprylic acid ( $C_8$ ), capric acid ( $C_{10}$ ), lauric acid (C<sub>12</sub>), myristic acid (C<sub>14</sub>), palmitic acid (C<sub>16</sub>), (Fig. 1b), stearic acid (C<sub>18</sub>), (Fig. 1c), arachidic (C<sub>20</sub>), behenic (C<sub>22</sub>), ligoceric  $(C_{24})$  and cerotic acid  $(C_{26})$  e.t.c. However, unsaturated fatty acids contain carbon chains with one or more double bonds in the hydrocarbon tail. The monounsaturated fatty acid contains only one double bond that is attached to the CH group and examples are: palmitoleic (C16:1), oleic acid (C18:1) (Fig. 1d) and eicosenoic acid (C20:1). While the poly unsaturated acid contains two or more Carbon to carbon double bonds (C=C). Examples are linoleic acid (C18:2) (Fig. 1e) and linolenic acid (C18:3) (Fig. 1f). Saturated fatty acids are solid at room temperature with high melting point while unsaturated ones are liquid at room temperature with lower melting point.

Saturated fatty acids have perfectly straight chain structure whereas the unsaturated ones are typically bent, unless they have a trans-configuration.

#### 2.2. Determination of fatty acid profile of the vegetable oil

The fatty acid compositional analysis was done by using Agilent, HP 6890 Gas Chromatograph with Flame ionization detector and 6890 Auto Sampler that connects with a controller box (Fig. 2). Gas chromatography technique is used for separation and detection of various molecular weight compound in the gas phase. The HP 6890 gas chromatograph equipped with flame ionization detector has a robust mechanism for correct analysis of fatty acids present in the vegetable oil samples. It has an electronic pneumatic control system for all gas pressures and flow rates and an on-board sensor that compensate for ambient temperature changes in the range of +4 °C to 450 °C. The automatic injector system and oven cryocooling gives room for exact measurement of retention attributes of volatile compound for accurate estimation of their physical properties.

The triglyceride in the oil was esterified by using an alkylation derivatization reagent (sodium methoxide) because fatty acids present in oils may be difficult to analyse in their free state due to their high polarity and formation of hydrogen bonds that consequently result in adsorption problems. Hence, methylation reduces fatty acids polarity and methyl esters offer better stability and quick quantitative samples for gas chromatography analyses. The fatty acid methyl ester was re-dissolved in 100  $\mu$ L hexane and 5  $\mu$ L volume of the samples were injected into GC-FID for separation and quantification. The carrier gas consists of a low molecular weight helium that is chemically inert and it serves as the mobile phase with flow rate of 1 ml/min.

The separation was done by HP-5 mm column coated with a stationary phase. When pressure was applied, the carrier gas helped to transfer the sample from the injector through the column into the flame ionization detector. The initial temperature was set at 100 °C and adjusted until the injector and detector temperatures were at 260 °C and 280 °C respectively. In the ionization detector, the sample was burnt to produce ion and free electrons which produces measurable current flow in the gap between the 2-electrodes inside the detector.



Fig. 1f. Cis, cis, cis, Linolenic acid (poly unsaturated).

The percentage of fatty acid methyl ester was calculated from the Gas chromatography graph by running the internal standard with the samples and taken into consideration the response factor of the different fatty acid methyl esters. (See Fig. 2.)

#### 2.3. Free fatty acids value determination

The free fatty acid in the vegetable oil was determined by chemical titration method (AOAC, 1990).

#### Crude coconut and palm kernel oil

Seven grams of well-mixed sample of coconut and palm kernel oil was measured into a 250 ml Pyrex Erlenmeyer flask. About 50 ml of ethyl alcohol (95% ethanol) which was previously neutralized by adding 2 ml phenolphthalein indicator solution and considerable amount of 0.1 M NaOH to produce faint permanent pink colour was then added to the oil in the flask. The reaction mixture was then titrated with 0.25 M NaOH solution and shaken rigorously until permanent faint pink which persists for less than sixty seconds was observed. Refined soya bean, corn, olive and canola oil

Fifty-six grams of well-mixed sample of each refined vegetable oil was accurately measured into a 300 ML Erlenmeyer flask. Also, 50 ML of ethyl alcohol (95% ethanol) containing 2 ML of phenolphthalein indicator was heated to a temperature of 60 °C by using water bath to prevent evaporation because ethanol boils at 78 °C. The mixture of hot, neutralized ethanol was then added to the vegetable oil in the flask and titrated with 0.1N sodium hydroxide solution (NaOH). The mixture was shaken constantly until a pink colour which persisted for thirty seconds (30 s) was observed in the alcohol layer above the sample.

#### Calculations

The coconut oil and palmkernel oil free fatty acids percentages were calculated in terms of % lauric acid by (1).

Free fatty acid (%) = 
$$\frac{V \times N \times 20}{W}$$
 (1)

However, the soyabean oil, corn oil, olive oil and canola oil free fatty acids (%) were calculated in terms of % oleic by using Eq. (2).

Free fatty acid (%) = 
$$\frac{V \times N \times 28.2}{W}$$
 (2)



Fig. 2. Agilent, HP 6890 gas chromatograph with flame ionization detector and 6890 auto sampler (Gentechscientific.com, 2018).

Where V = volume in ml of standard sodium hydroxide solution used

N = normality of standard sodium hydroxide solution used W = mass (g) of oil sample used.

#### 2.4. Production of fatty acid methyl esters (FAMEs)

#### Transesterification process

Trans-esterification reaction is the main process of converting triglycerides present in vegetable oil to alky esters by using alcohol in the presence of sodium, potassium hydroxide or lipase catalyst and under optimum condition (Zhou et al., 2003; Rashid et al., 2008; Anawe and Folayan, 2018b).

The optimum conditions put forward by various researchers towards efficient conversion of fatty acids to methyl esters are: catalyst concentration of 1.5% for potassium hydroxide (KOH) and 1.0% for sodium hydroxide (NaOH), alcohol to oil molar ratio of 6:1 for methanol and 9:1 for ethanol, reaction temperature of 60–65 ° C and reaction time of 2–3 h (Encinar et al., 2007; Al Naggar et al., 2017; Anawe and Folayan, 2018c).

#### Process methodology

The coconut and palm kernel oil were bought in appreciable quantities from Badagry, a suburb of Lagos, Nigeria. While about five litres (5) each of refined soyabean oil, corn oil, olive oil and canola oil were purchased from varieties store in Lagos. The vegetable oils were filtered to remove suspended solid particles that can adversely affect the biodiesel process. The level of free fatty acids present in each oil was determined by chemical titration method because vegetable oil with free fatty acid content above 2.0%–2.5%, requires an acid esterification as a treatment stage to reduce the level of Free Fatty Acid content (FFA) before the main transesterification reaction (Tomasevic and Silermarinkovic, 2003).

Hence, 1000 ml of each vegetable oil was measured by measuring cylinder and poured into six (6), 2500 ml Pyrex-Erlenmeyer flask. The oil was heated by using heating mantle to a temperature of 60 °C. A sodium methoxide solution

prepared by dissolving 18 g of sodium hydroxide (NaOH) in 160 ml of methanol (analytical grade) and at a temperature of 50 °C was quickly transferred into the flask containing the heated vegetable oil. The mixture was stirred on a magnetic stirrer at temperature of 65 °C for the reaction to reach completion. After two hours (2 h), distilled water of about 15% of initial volume of oil used was added to the system and the mixture was transferred from the flask to a two-litre separating funnel and allowed to stand overnight.

A two distinct layer of mono alkyl ester (biodiesel) and glycerol was observed with the glycerol setting at the bottom of the funnel due to its higher density. The glycerol was removed through the bottom opening of the funnel while the methyl ester was decanted into a 1000 ml flask for purification. Warm water at 40 °C and about 20% by volume of the produced ester was used to wash the biodiesel in order to remove the alcohol and excess catalyst present in the biodiesel.

Finally, the ester was dried by using magnesium chloride  $(MgCl_2)$  in order to remove any free moisture present.

**Note**: For the coconut oil and palm kernel oil with free fatty acid content of 10.60 and 5.2% respectively (Table 4), an acid esterification was done as a preliminary step to reduce the free fatty acids to acceptable levels before the main transesterification reaction.

#### 2.5. Fuel properties evaluation methods

The saponification Number (S.N) and Iodine value (I.V) of the vegetable oils and their fatty acid methyl esters (FAMEs) were calculated from Eqs. (3) and (4) proposed by kalayasiri et al. (1996) and validated by Mohibbe et al. (2005).

The advantage of these equations is that the relative contributions of each fatty acid to the total S.N and I.V can be easily evaluated.

Saponification number (S.N) = 
$$\sum \left[\frac{(560 \times A_i)}{Mw_i}\right]$$
 (3)

Iodine Value (IV) = 
$$\sum \left[ \frac{(254 \times D \times A_i)}{Mw_i} \right]$$
 (4)

Where  $A_i$  is the percentage composition of each fatty acid in the vegetable oil or its ester, D is the number of double bonds present in each unsaturated fatty acid or its ester and  $Mw_i$  is the molecular weight of each fatty acid or its ester component.

Similarly, the cetane number (CN) and higher heating values (HHVs) were also evaluated by using Eqs. (5) and (6) as reported by Krisnangkura (1986) and Demirbas (1998) respectively.

Cetane number (CN) = 
$$46.3 + \left(\frac{5458}{5.N}\right) - (0.225 \times IV)$$
 (5)

Higher Heating Value (HHV) =  $49.43 - (0.041 \times S.N) - (0.015 \times IV)$  (6)

#### 3. Results and discussion

#### 3.1. Fatty acids compositional analyses

The results of the fatty acid components and percentage composition of each vegetable oil as determined from gaschromatograph equipped with flame ionization detector are shown in Tables 1a–1c. It can be inferred that the coconut and palm kernel oil consist of higher percentages of saturated fatty acids than the unsaturated ones with lauric acid constituting the bulk of saturation (Table 1a). The major source of unsaturation in the two vegetable oils is the oleic acid with palm kernel oil having more percentage of monounsaturated fatty acid than the coconut oil. The soyabean and corn oil have more poly unsaturated fatty acids in their profile though with appreciable percentage of oleic acid. This results in higher degree of unsaturation (Table 2). Whereas, the oleic acid constituted the bulk of unsaturation in olive and canola oil.

#### 3.2. Cold flow properties

One of the major catastrophes that is associated with the use of biodiesel in direct-injection, compression ignition engines, is poor low temperature flow properties which are indicated by relatively high cloud and pour points (Dunn and Knothe, 2001; Knothe et al., 2001; Durret et al., 2003).

The cold flow properties of fuels (paraffinic and Fatty acid alkyl esters) are typically concerned with the performance characteristics of the fuel under low temperature climatic conditions. These properties can affect fuel flow and the performance of fuel pump, filter and injector. About four parameters are used to quantify the dynamic behaviour of fuel under varying temperature conditions. These are, cloud point, pour point, cold filter plugging point (CFPP) and low temperature filterability test (LTFT). The cloud point is the temperature at which the formation of waxy structures in a fuel becomes visible as the liquid temperature is lowered. It is the temperature at which crystals becomes visible and form a cloudy suspension as the oil is cooled during cold temperature because the oil components having high melting point will agglomerate and nucleate to form solid crystals. The pour point represents the lowest temperature at which the fuel can flow or be pumped having solidified enough to resist flow. The pour points (PP) and the cloud points (CP) were determined by using the American Standard for Testing Materials procedures.

However, the cold filter plug point and low-temperature filterability test were incorporated to cold flow properties and performance evaluation because of the failure of cloud point and pour point to correctly predict the performance of biodiesel during cold weather operations (Gaurav et al., 2016). While the cold filter plugging point (CFPP) is the temperature at which the fuel will solidify and block the flow of fuel through the filter, the Low temperature filterability test was developed to predict limiting fuel temperatures in a better where start up and operability complications may be expected after fuel's exposure to cold climate environment. The CFPP is the most observed cold flow parameter because it mainly affects fuel adsorption in lower temperature range.

The cold flow properties of vegetable oils and its Alkyl esters (biodiesel) are primarily dependent on fatty acid composition of the parent oil, either saturated or unsaturated, length of fatty acid (short chain, medium or long), amount of mono and poly unsaturated fatty acid, degree of saturation and long chain saturation factor (Verissimo et al., 2011; Hoekman et al., 2012; Echim et al., 2012). Inferior cold flow properties of biodiesel can cause gum formation and crystallization of fuel particles and adversely affect fuel flow, pump and injector (Bello et al., 2015).

The coconut and palm kernel oil have low percentage of unsaturated fatty acids and larger percentage of saturated acids in their fatty acid profiles as determined from GC-FID analysis (Table 1a) and thus poor cold flow properties (Table 6) because saturated fatty acids tend to crystallize at higher temperature and they are usually associated with high melting point and thus forms crystals easily during in cold temperature. Whereas the corn oil biodiesel and soyabean biodiesel have a comparatively higher percentage of unsaturated fatty acid (Table 2) and thus better cold flow behaviour. Vegetable oils having more saturation will result in biodiesel with poor cold flow properties. The methyl ester of coconut and palm kernel oil have a relatively high cold filter plugging point (CFPP) because CFPP increases with amount and carbon chain length of saturated fatty acids Alkyl esters. The temperature at which fatty acid alkyl ester begins to crystallize is usually greater than that of paraffinic diesel. Hence, Crystallization at higher temperature can result in clogging of fuel pipes thus complicating the pumping ability of fuel and affects engine operation in winter (Smith et al.)

Saturated fatty acids form crystals during cold weather operations which unarguably results in clogging of fuel filters and lines, thus causes improper engine operation during cold temperature working condition (Verma et al., 2016). Similarly, the formation of a cloudy-wax like structure results in improper engine operation because the solidified substance blocks the fuel pipes and results in flow inability. Degree of unsaturation has significant impact on biodiesel pour and cloud points, as more unsaturation results in better cold flow performance.

The soyabean and corn oil methyl esters (biodiesel) have higher percentage of linoleic acid (Table 1b) resulting in higher degree of unsaturation. This gives room for better cloud point, pour point, cold filter plug point and low temperature filterability test (Table 6). The existence of double bonds in the Oleic and linoleic acid form a cis-cis configuration which reduces intermolecular attraction and thus lowers the melting point. The olive and canola oil consist majorly of omega-9-fatty acid (Oleic), poly unsaturated omega-6-fatty acid (linoleic) and specifically alpha poly unsaturated omega-3-fatty acids.

The structure of the fatty acids is another important parameter that influences cold flow behaviour of biodiesel. Fatty acids differ by length and can also be classified as short-chain fatty acids (SCFAs), (C1–C5), Medium chain fatty acids (MCFAs), (C6–C12), long chain fatty acids (LCFAs) (C13–C21) and very long-chain fatty acids (VLCFA) (C22 & above) (Table 3). From Table 7, the melting point increases with chain length and reduces when the number of double bond increases. Long chain fatty acid that are saturated are usually solid at room temperature and their melting point increases as chain length increases. Whereas unsaturated fatty acids are liquid at room temperature with relatively lower melting point.

In summary, vegetable oils that consist of fatty acids with more long chain carbon atoms (C13 & above) than medium or short chain carbons will definitely have poor cold flow properties

#### Table 1a

	Fatty acid	composition	of coconu	t and	palmkernel	oil	from	GC-FID	analysis.
--	------------	-------------	-----------	-------	------------	-----	------	--------	-----------

Fatty acid (%)	Molecular formular	Molecular structure	Structural formular	Coconut oil	Palmkernel oil
Saturated					
Caproic	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	6:0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH	0.59	0.4
Caprylic	$C_8H_{16}O_2$	8:0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> COOH	8.10	3.80
Capric	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	10:0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOH	6.50	4.00
Lauric	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	12:0	$CH_3(CH_2)_{10}COOH$	47.00	49.50
Myristic	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	14:0	$CH_3(CH_2)_{12}COOH$	18.60	14.90
Palmitic	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	16:0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH	8.40	7.80
Stearic	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	18:0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	2.6	2.50
Arachidic	$C_{20}H_{40}O_2$	20:0	$CH_3(CH_2)_{18}COOH$	0.10	0.10
Unsaturated					
Oleic	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	18:1	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	6.4	14.70
Linoleic	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	18:2	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH=CHCH <sub>2</sub> CH=CH(CH <sub>2</sub> ) <sub>7</sub> COOH	1.60	2.20
Linolenic	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	18:3	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$	0.1	-

#### Table 1b

Fatty acid composition of soyabean and corn oil from GC-FID analysis.

Fatty acid (%)	Molecular formular	Molecular structure	Structural formular	Soyabean oil	Corn oil
Saturated					
Lauric	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	12:0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH	0.10	-
Myristic	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	14:0	$CH_3(CH_2)_{12}COOH$	0.20	0.17
Palmitic	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	16:0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH	10.50	12.10
Stearic	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	18:0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	3.80	2.30
Arachidic	$C_{20}H_{40}O_2$	20:0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>18</sub> COOH	0.30	-
Behenic	$C_{22}H_{44}O_2$	22:0	$CH_3(CH_2)_{20}COOH$	0.28	-
Unsaturated					
Palmitoleic	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	16:1	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	-	0.12
Oleic	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	18:1	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	23.70	30.90
Linoleic	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	18:2	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7$ COOH	54.50	53.30
Linolenic	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	18:3	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7$ COOH	6.30	1.10
Erucic	C <sub>22</sub> H <sub>42</sub> O <sub>2</sub>	22:1	$CH_3(CH_2)_7CH=CH(CH_2)_{11}$ COOH	0.25	-

#### Table 1c

Fatty acid composition of olive and canola oil from GC-FID analysis.

Fatty acid (%)	Molecular formular	Molecular structure	Structural formular	Olive oil	Canola oil
Saturated					
Myristic	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	14:0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> COOH	0.01	0.18
Palmitic	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	16:0	$CH_3(CH_2)_{14}COOH$	13.60	4.35
Stearic	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	18:0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	2.70	2.00
Arachidic	$C_{20}H_{40}O_2$	20:0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>18</sub> COOH	0.50	0.50
Behenic	$C_{22}H_{44}O_2$	22:0	$CH_3(CH_2)_{20}COOH$	0.12	-
Ligoceric	$C_{24}H_{48}O_2$	24:0	$CH_3(CH_2)_{22}COOH$	0.60	-
Unsaturated					
Palmitoleic	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	16:1	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	1.65	0.275
Oleic	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	18:1	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	68.20	59.40
Linoleic	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	18:2	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7$ COOH	11.50	21.15
Linolenic	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	18:3	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7$ COOH	0.90	10.35
Eicosenoic	C <sub>20</sub> H <sub>38</sub> O <sub>2</sub>	20:1	$CH_3(CH_2)_7CH=CH(CH_2)_9COOH$	0.20	0.80
Erucic	$C_{22}H_{42}O_2$	22:1	$CH_3(CH_2)_7CH=CH(CH_2)_{11}$ COOH	-	0.78

#### Table 2

Distribution of saturated and unsaturated fatty acids in the oil samples.

Components	Coconut oil	Palmkernel oil	Soyabean oil	Corn oil	Olive oil	Canola oil
SFAs (%)	91.89	83.00	15.18	14.57	17.53	7.03
MUFAs (%)	6.40	14.70	23.95	31.02	70.05	61.25
PUFAs(%)	1.70	2.20	60.80	54.40	12.40	31.50
Total USFAs (MUFAS+PUFAS)	8.10	16.90	84.75	85.42	82.45	92.75
DU	9.80	19.10	145.55	139.82	94.85	124.25
LSCF	2.24	2.13	3.61	2.36	4.59	1.94

SFAs = saturated fatty acids, MUFAs = monounsaturated fatty acids, PUFAs = poly unsaturated fatty acids, USFAs = unsaturated fatty acids, DU = degree of unsaturation, LCSF = long chain saturation factor.

because of easy crystallization at higher temperature. Branched chain fatty acids have good cold flow properties because of lower temperature requirement for crystallization. In saturated acids, odd-chains acids have low melting points than even chain ones because the cis-configuration or the presence of –OH groups in the chain reduces the melting point.

One important method of improving cloud point is the reduction of saturation content of the vegetable oil. Other methods that

Table 3

Carbon length distribution of saturated and unsaturated fatty acids in the oil samples.

Length of carbon	Coconut oil	Palmkernel oil	Soyabean oil	Corn oil	Olive oil	Canola oil
SCFA (C1-C5)	NP	NP	NP	NP	NP	NP
MCFA (C6-C12)	62.19	57.70	0.10	NP	NP	NP
LCFA (C13-C21)	37.80	42.20	99.58	99.99	99.26	99.01
VLCFA (C22 & above	NP	NP	0.25	NP	0.72	0.78

SCFA = short-chain fatty acid, MCFA = medium-chain fatty acid, LCFA = long-chain fatty acid, VLCFA = very long chain fatty acid, NP = not present.

I	Free fatty acids (%) of vegetable oil use	d for the experiment.
	Oil sample	% Free fatty acid
	Crude coconut oil	10.6% of lauric acid
	Crude palm kernel oil	5.20% of lauric acid
	Refined Soya bean oil	0.60% of oleic acid
	Refined Corn oil	9999.55% Of oleic acid
	Olive oil	0.74% of oleic acid
	Canola oil	0.80% of oleic acid

Table 5

ASTM D6751-07b and EN 14214 standard specification (American Society for Testing Materials, 2007; European committee for standardization, 2003).

Test property	Test method	EN standard	ASTM standard
Kinematic viscosity @ 40 °C (mm <sup>2</sup> /s)	ASTM D445	3.5–5	1.9–6.0
Specific gravity @ 15 °C	ASTM D1298	0.86-0.9	0.88
Flash point (°C)	ASTM D93	120 min	130 min.
Pour point (°C)	ASTM D5853	-15 to 6	—10 max.
Cloud point (°C)	ASTM D2500	Report	Report
CFPP (°C)	ASTM D6371	Report	Report
LTFT (°C)	ASTM D4539	Report	Report
Cetane Number	ASTM D613	51 min	47 min.
Calorific value kj	ASTM D240	35 MJ/Kg	Sufficiently close to diesel
Iodine value $\frac{gl_2}{100 \text{ g of biodiesel}}$	ASTM D445	120 max	Report
Acid number $\left(\left(\frac{\text{mgKOH}}{g}\right)\right)$	ASTM D664	0.50 max	0.80 max
Sulphated ash (%)	ASTM D 874	0.02 max	0.02 max.
Free glycerin	ASTM D6584	0.02 max	0.02 max
Oxidation Stability	EN14112	3 h	6 h
Copper strip corrosion	D130	No 1 max	No 3 max

can used for improvement of cold flow behaviour are blending of the biodiesel with conventional petrol diesel, transesterification of the parent vegetable oil with branched chain alcohol e.g Isopropanol, winterization, use of chemical additives e.g pour point depressant and finally, modification of the fatty acids profiles of the vegetable oil. Enzymatic acidolysis can also be used to lower cloud points of biodiesel (Khalid et al., 2011). Similarly, Stephen and Naoko (2013) have also proposed the use of isomerization and hydro-isomerization as a panacea to improving the cold flow properties of biodiesel.

Summarily, the longer the carbon length of fatty acids, the better the cold flow behaviour. Also higher degree of unsaturation results in better cold flow properties.

#### 3.3. Saponification number (SN)

The saponification number is the weight of potassium hydroxide that is required to break the ester bonds between fatty acids and glycerol present in one gram of fat and oil. That is, it is the amount of KOH in milligram that is required to convert one gram of fat into soap or glycerine. It is a measure of the average molecular weight and chain length of all fatty acid present. The long chain fatty acids have a low saponification number because of presence of fewer number of carboxylic functional group per unit mass of the fat in comparison with short chain fatty acid.

The coconut and palm kernel oil have shorter and medium chains hydrocarbon lengths than the other vegetable oil samples (Table 3). This results in higher saponification number of both



Fig. 3a. Percentage contribution of fatty acids to coconut oil biodiesel saponification number.

the parent oil and its biodiesel as observed in Tables 8 and 9 because saponification number has an inverse relationship with both molecular weight and carbon chain length.

Table 6				
Cold flow properties of biodiesel	produced fi	rom the	various oil	samples.

Cold flow property	Coconut biodiesel	Palmkernel biodiesel	Soyabean biodiesel	Corn oil biodiesel	Olive oil biodiesel	Canola oil biodiesel
Cloud point (°C)	4.5	3.6	-3	-2.5	-1	-2
Pour point (°C)	-3	-1.7	-9	-6.5	-4	-6
Cold filter plug point (°C)	2.5	1.5	-7	-5.	-2	-4
Low temperature filterability test ( $^{\circ}C$ )	5	4	-3	-2	1	-1

a	h	le	7
	~		

т

Melting point of some saturated and unsaturated fatty acids and their methyl esters.

Fatty acid	Configuration	Molecular weight	Melting point (°C)
Caprylic acid	8:0	144.2	16.50
Methyl ester	8:0	158.2	-
Capric acid	10:0	172.3	31.5
Methyl ester	10:0	186.3	-
Lauric acid	12:0	200.3	44
Methyl ester	12:0	214.3	5
Myristic acid	14:0	228.4	58
Methyl ester	14:0	242.4	18.5
Palmitic acid	16:0	256.4	63
Methyl ester	16:0	270.4	30.5
Stearic acid	18:0	284.5	71
Methyl ester	18:0	298.5	39
Oleic acid	18:1	282.5	16
Methyl ester	18:1	296.5	-20
Linoleic acid	18:2	280.5	-5
Methyl ester	18:2	294.5	-35
Linolenic acid	18:3	278.4	-11
Methyl ester	18:3	292.5	-57/-52

However, the relative contribution of each fatty acid component to the saponification number of each biodiesel is shown in Figs. 3a–3f. In coconut and palm kernel oil, the lauric acid contributed highest percentage of 48.28% and 53.02% to the saponification number respectively (Figs. 3a and 3b). while arachidic acid made the lowest contribution in both oil.

Whereas, linoleic acid accounts for 54.14% and 52.83% of the saponification number in soyabean and corn oil biodiesel respectively (Figs. 3c and 3d). The palmitoleic acid contributed the least value in corn oil while erucic acid in soyabean oil. The oleic acid was responsible for 67.31% and 59.22% of the total saponification number in olive and canola oil biodiesel respectively (Figs. 3e and 3f). While the lowest values come from myristic acid to the biodiesel.

In summary, the higher the carbon length, the lower the saponification number because saponification number has an inverse relationship with both molecular weight and carbon length.

Similarly, the higher the degree of unsaturation, the lower the saponification number. Coconut and palmkernel oil with lower degrees of unsaturation of 9.80 and 19.10 respectively (Table 2) have higher saponification values of 272.6  $\pm$  1.36 and 264.6  $\pm$  1.32 respectively for the parent oil (Table 9). While the methyl ester has saponification values of 254.2  $\pm$  1.27 and 243.9  $\pm$  1.22 respectively (Table 10). However, soyabean with a very high degree of unsaturation of 145.55(Table 2) has a saponification value of 201.4  $\pm$  1.00 for its raw oil (Table 9) and 191.4  $\pm$  0.96 for its fatty acid methyl ester (Table 10).

#### 3.4. Iodine value (IV)

The iodine value is the amount of iodine measured in grams that is absorbed by 100 ml of a given oil or biodiesel and it is a key indicator of the degree of unsaturation of the oil. Biodiesel with low iodine value are generally more combustible and efficient fuel than those with higher values but may have poor cold flow properties (Uriate, 2010). It provides us useful information about the degree of unsaturation of the oil that directly affects its stability to oxidation (Adekunle et al., 2016). When biodiesel containing higher amount of unsaturated fatty acid is heated, polymerization of glycerides occurs which can result in deposit formation and thus deteriorates the fuel's lubrication property (Salles et al., 2010). Hence, a maximum iodine value of 120  $gI_2/100$  g of biodiesel is recommended by EN14214 biodiesel standard (Table 5). From Table 1a, the coconut and palm kernel oil contain fewer amount of unsaturated fatty acid and hence lower degree of unsaturation. This invariably corresponds to lower iodine values compare with other oil samples with higher degree of unsaturation. The graphical representation of the contribution of each unsaturated fatty acid to the iodine value of different samples of biodiesel is shown in Figs. 4a-4f. While the oleic acid contributed larger percentage of 64.47 and 76.82% to the coconut and palm kernel oil biodiesel respectively (Figs. 4a and 4b), linoleic accounted for larger contributions of 71.82% and 75.98% of the total iodine value in soyabean and corn oil respectively (Figs. 4c and 4d). However, in the olive and canola oil biodiesel, the oleic acid was responsible for larger parts of the iodine value with percentage contribution of 70.96% and 43.95% respectively (Figs. 4e and 4f). Iodine value increases with degree of unsaturation but decreases with chain length.

lodine value has a positive linear relationship with carbon length. The higher the carbon length, the higher the iodine value. The coconut and palmkernel oil consist essentially of medium chain fatty acids (MCFAs) of carbon length range (C6–C12) as shown in Table 3 and thus lower iodine values (Tables 9 and 10). Whereas, other oil that contains entirely of Long chain fatty acids (LCFAs) of carbon length range (C13–C21) has higher iodine values.

#### 3.5. *Cetane number (CN)*

The cetane number (CN) gives the numerical indication of the ignition quality of the fuel. Higher cetane number corresponds to better ignition quality (Azam et al., 2005). This numerical quantity is related to the ignition delay (ID) time which is the time elapse between the injection of the fuel into the cylinder and onset of ignition. The higher the CN, the shorter the ID time





Fig. 3c. Percentage contribution of fatty acids to soyabean oil biodiesel saponification number.



Fig. 3d. Percentage contribution of fatty acids to corn oil biodiesel saponification number.



Fig. 3e. Percentage contribution of fatty acids to olive oil biodiesel saponification number.



Fig. 3f. Percentage contribution of fatty acids to canola oil biodiesel saponification number.





Fig. 4a. Graphical Representation of Fatty Acids Contribution to Iodine Value of Coconut Oil Biodiesel.

and the better the ignition quality (Knothe, 2005a). The value of the cetane number is a sacred function of the following three (3)

Fig. 4b. Graphical representation of fatty acids contribution to iodine value of palm kernel oil biodiesel.

important parameters. (1) percentage of unsaturated fatty acids components or simply put it as the degree of unsaturation (2)



Fig. 4c. Graphical representation of fatty acids contribution to iodine value of soyabean oil biodiesel.



Fig. 4d. Graphical representation of fatty acids contribution to iodine value of corn oil biodiesel.



Fig. 4e. Graphical representation of fatty acids contribution to iodine value of olive oil biodiesel.

the number of double bonds present in the fatty acid of the oil and (3) The molecular weight of the fatty acid which have a direct relationship with the length of the carbon atoms or the carbon chains (Lamaisiri et al., 2015). Generally, cetane number increases with chain length (Klopfenstein, 1985).

A cetane number of minimum value of 47 is recommended by the United states (ASTM D6751) while the European recommends



Fig. 4f. Graphical representation of fatty acids contribution to iodine value of canola oil biodiesel.

a minimum value of 51 (Table 5) as against the 45 minimum value proposed by the Brazillian biodiesel standard.

The coconut and Palm kernel oil biodiesel have an exceptionally high cetane number of 65.85  $\pm$  0.99 and 65.10  $\pm$  0.98 as observed in Table 10 because of higher percentage of saturated fatty acids in their fatty acid profile as determined from gas chromatography technique. In these two oils, lauric acid, myristic and palmitic acid constitute the bulk of the fatty acids (Table 1a) and thus lower degrees of unsaturation as shown in Table 2. Saturated methyl esters are generally known to have higher cetane number. For instance, the cetane number of methy ester of lauric acid is 61.1, myristic is 69.9, palmitic (74.4) and stearic is 76.30. whereas oleic methyl ester has cetane index of 57.2 linoleic (36.8) and linolenic (21.6) (Bangboye and Hansen, 2008). Similarly, Knothe et al. (2003) measured the cetane number of palmitic acid methyl ester to be 85.9, stearic is 101 while oleic and linoleic are 59.3 and 38.2 respectively. Hence, biodiesel consisting principally of esters of lauric, myristic, palmitic and palmitic acid will have higher cetane number than those with oleic, linoleic and linolenic acid as chief constituents.

Meanwhile, the corn oil biodiesel has a higher cetane index of  $47.58 \pm 0.71$  compared to that of the soya bean oil of  $45.51 \pm 0.68$  (Table 10). Increasing number of double bonds lowers cetane number as it can be observed in soyabean oil and its methyl ester (Tables 9 and 10) compared to that of corn oil. Due to higher proportion of linolenic acid (18:3) in the soyabean fatty acid profile (about 6.30%) as against that of corn oil of only 1.10% (Table 1b). This higher degree of unsaturation coupled with higher percentage of polyunsaturated fatty acid makes the soyabean oil have a lower cetane number than the corn oil.

Similarly, the canola oil and its biodiesel have a higher degree of unsaturation with larger percentage of poly unsaturated fatty acid than the olive oil (Table 2). This consequently result in lower cetane number. Cetane number increases with chain length and decreases with higher degree of branching.

Generally, the esters of highly unsaturated fatty acids such as linoleic (18:2) and linolenic (18:3) are usually associated with long ignition delay times due to low cetane number. This ultimately results in poor combustion.

The degree of deviation of the cetane number predicted by using Eq. (5) from the measured value by ASTM D 613 was quantified by using percentage error (Table 8). As a result of this, the coconut oil biodiesel has the lowest percentage error of 0.6787% while palmkernel oil biodiesel has the highest percentage error of 4.16% (Table 8). There is no marked deviation of the calculated biodiesel cetane numbers from their measured values.

1				
Biodiesel	Measured C.N	Calculated C.N	Absolute error	Error (%)
Coconut	66.30 ± 1.04	$65.85 \pm 0.99$	0.45	0.6787
Palmkernel	$62.50 \pm 0.94$	$65.10 \pm 0.98$	2.60	4.1600
Soyabean	$47.00 \pm 0.71$	$45.51 \pm 0.68$	1.49	3.1702
Corn	$48.20 \pm 0.72$	$47.58 \pm 0.71$	0.62	1.2863
Olive	$58.60 \pm 0.88$	$56.44 \pm 0.85$	2.16	3.6860
Canola	$48.50 \pm 0.73$	$49.20 \pm 0.74$	0.7000	1.4433

Comparison of measured and calculated cetane number (CN).

#### 3.6. *Higher heating values (HHVs)*

Table 8

Heating value is the amount of heating energy that is released by the combustion of a unit volume of fuel. It is concerned with the energy content and the amount of fuel that an engine will consume. Higher heating value corresponds to lower fuel consumption and vice versa (Knothe et al., 1998). The amount of moisture content is the principal determinant of heating value. Higher heating value also increases with viscosity (Demirbas, 2008). It also increases with an increase in chain length but decreases with an increase in degree of unsaturation (double bonds). The coconut and palm kernel oil have low higher heating values regardless of its low degree of unsaturation because of the presence of more medium chain fatty acids. Oleic acid methyl ester has higher heating value than linoleic and linolenic methyl esters. Olive and canola oil have higher percentage of oleic acid methyl ester and hence higher heating values than soyabean and corn oil biodiesel with higher percentage of linoleic acid. Biodiesel heating value increases with increasing carbon number in the ester molecule as well as with increasing ratio of carbon to hydrogen and nitrogen atoms (Demirbas, 1997).

#### 3.7. Density

Fuel density is the principal controlling factor of engine performance characteristics because it is concerned with the mass of biodiesel that is injected into the combustion chamber and thus air-fuel ratio. Density depends on fatty acid composition of the vegetable oil, its method of extraction and efficiency of the biodiesel process. Density increases with decreasing chain length and increasing number of double bonds (Rafaat, 2009).

#### 3.8. Kinematic viscosity (K.V)

Viscosity is one of the most important factors that affect biodiesel performance in diesel engines. It has a direct implication on fuel atomization, lubricity, impinging distance as well as burning efficiency of a liquid fuel (Cherng and Lin, 2012). Biodiesel with high viscosity tends to form larger droplets on injecting the fuel which can undoubtedly cause poor fuel atomization during the spray, increases engine deposits, wearing of fuel pumps and injectors due to more energy requirement, poor combustion, increase exhaust smoke and emission (Knothe and Steidley, 2005b)

Viscosity increases with chain length (number of carbon atoms) because of increased number of random intermolecular interactions. Viscosity also increases with increasing degree of unsaturation and it is also influenced by the configuration of the double bond with the trans having a higher viscosity than the cis-configuration (Knothe, 2005b).

Branching is another phenomenon that can affect viscosity because it reduces the interaction between carbon chains by hindering neighbouring molecules approach (Lee et al., 1995).

The coconut and palm kernel oil and their biodiesel have relatively lower viscosity values at 40  $^{\circ}$ C (Tables 9 and 10) than other vegetable oil not minding the fact that they have higher

degrees of saturation because they consist chiefly of medium chain fatty acids (Table 3) and viscosity has a positive linear relationship with chain length. However, the soyabean, corn, olive and canola oil biodiesel have higher viscosities because the parent oil has fatty acids components that are made up of long carbon chains. This scenario suggests that carbon chain length has a more pronounce effect on kinematic viscosity than degree of saturation. All the biodiesel kinematic viscosity values fall within ASTM D6751 requirement of 1.9–6.0 mm<sup>2</sup>/s and European standard of 3.5–5 mm<sup>2</sup>/s as shown in Table 5.

#### 3.9. Flash point

The flash point of a fuel measures the tendency of a fuel to form a flammable mixture in air. It is the lowest temperature at which a liquid fuel will vaporize to form an ignitable mixture in air. It has a direct positive relationship with fluid's viscosity. All the produced biodiesel specimen falls within the standard flash point requirement.

Flash point is useful in determining the transportation and storage requirement of biofuels. The flash point should high enough to ensure safe operation and reduced vaporization within the maximum operating temperature (Nadia et al., 2013).

#### 4. Conclusion

The effect of fatty acid configuration, chain length, branching and degree of unsaturation on cold flow and critical properties of biodiesel was experimentally studied by synthesis of fatty acid methyl esters (FAMEs) from six different vegetable oil biomass via alkali catalyzed transesterification reaction.

The following important conclusions can be drawn based on the results obtained.

- The lauric oils (coconut and palm kernel oil) have higher pour point, cloud point, cold filter plugging point and low temperature filterability test point compared to the oleic and linoleic oils which results in poor cold flow behaviour because these properties significantly improved with higher degree of unsaturation, longer chain length, higher degree of branching and with cis configuration.
- Saponification number decreases with chain length and molecular weight. Also increasing degree of unsaturation reduces the saponification number.
- The iodine value increases as the degree of unsaturation increases but decreases with chain length.
- Cetane number increases with chain length and degree of saturation but decreases with higher degree of branching
- The higher heating values (HHV) have a linear positive relationship with chain length but decreases with higher degree of unsaturation. Oleic acid methyl ester has a higher heating value than linoleic and linolenic methyl esters.
- The kinematic viscosity increases with chain length and increasing degree of unsaturation and it is also influenced by

#### Table 9

Critical properties of various oil samples.

Test property	Coconut oil	Palmkernel oil	Soyabean oil	Corn oil	Olive oil	Canola oil
Kinematic viscosity @ 40 °C(mm <sup>2</sup> /s)	28.60	31.10	31.80	34.80	38.20	36.05
Specific gravity @ 15 °C	0.921	0.923	0.925	0.920	0.912	0.914
Flash point (°C)	228	212.50	248	265	216	241
Cetane number	$64.31 \pm 0.96$	$63.05 \pm 0.94$	$42.55 \pm 0.64$	$44.74 \pm 0.67$	$53.97 \pm 0.81$	$46.42\pm0.70$
Higher heating value Mj/kg	$38.12\pm0.48$	$38.32 \pm 0.48$	$39.11\pm0.49$	$39.24 \pm 0.49$	$39.85 \pm 0.50$	$39.43 \pm 0.49$
Iodine value $\frac{gl_2}{100 \text{ g of biodiesel}}$	$8.934\pm0.22$	$17.23 \pm 0.43$	$137.7 \pm 3.44$	$127.7\pm3.19$	$86.63 \pm 2.17$	$121.8\pm3.04$
Saponification number	$272.6\pm1.36$	$264.6 \pm 1.32$	$201.4\pm1.00$	$201.9 \pm 1.01$	$201.9\pm1.01$	$199.25 \pm 0.99$

#### Table 10

Critical properties of biodiesel produced from the various oil samples.

	-	-				
Test property	Coconut methyl ester	Palmkernel methyl ester	Soyabean methyl ester	Corn oil methyl ester	Olive oil methyl ester	Canola oil methyl ester
Kinematic viscosity @ 40 °C(mm²/s)	3.05	2.94	3.86	4.18	4.31	4.20
Specific gravity @ 15 °C	0.873	0.881	0.884	0.871	0.868	0.870
Flash point (°C)	146	132	181	119	114	158
Cetane number	$65.85\pm0.99$	$65.10\pm0.98$	$45.51\pm0.68$	$47.58 \pm 0.71$	$56.44\pm0.85$	$49.20\pm0.74$
Higher heating value $\frac{Mj}{kg}$	$38.88 \pm 0.48$	$39.18 \pm 0.49$	$39.62 \pm 0.50$	$39.74\pm0.50$	$40.35\pm0.50$	$39.94\pm0.50$
$\frac{\text{Iodine value}}{\frac{gl_2}{100 \text{ g of biodiesel}}}$	8.50 ± 0.21	$16.39\pm0.41$	130.9 ± 3.27	$121.4\pm3.04$	82.32 ± 2.06	115.8 ± 2.89
Saponification number	254.2 ± 1.27	243.9 ± 1.22	$191.4\pm0.96$	$191.8 \pm 0.96$	$191.4\pm0.96$	$189.5 \pm 0.95$

the configuration of the double bond with the trans having a higher viscosity than the cis-configuration.

• Density exhibited a positive correlation with degree of unsaturation but showed an inverse relationship with chain length.

#### **Reference data**

The authors can boldly say that all the data used in this study were gotten from rigorous experimental research in the laboratory and not from any journal either in print or on line. We also declare that the data will be available for public use once the paper is published.

#### Acknowledgements

The authors are very grateful to Chancellor of Covenant University and the university management team for their support in providing research enabling environment and condition.

#### **Funding statement**

The authors are grateful to Covenant University, Ota, Nigeria, for providing the fund required to carry out this research.

#### **Declaration of competing interest**

The authors are happy to say that there is no conflict of interest regarding the publication of this paper publication. The paper represents a unanimous purpose of interest.

#### References

- Adekunle, S.A., Oyekunle, A.O., Obisesan, R.O., Ojo, O.S., Ojo, S.O., 2016. Effects of degumming on biodiesel properties of some non-conventional seed oils. Energy Rep. 2 (2016), 188–193.
- Agarwal, A.K., 1998. Vegetable oils versus diesel fuel: development and use of biodiesel in a compression ignition. TERI Inf. Digest Energy 8, 191–203.

- Al Naggar, M.M., Ashour, F.H., Ettouney, R.S., El Rifai, M.A., 2017. Production of biodiesel from locally available spent vegetable oil. J. Renew. Energy Sustain. Dev. 3 (2), 189–195.
- American Society for Testing Materials, 2007. ASTM Standard Specification for Biodiesel Fuel (B100); Annual Book of ASTM Standards. ASTM International, West Conshohocken, Method D6751-07b.
- Anawe, P.A.L., Folayan, J.A., 2018a. Data on physico-chemical, performance, combustion and emission characteristics of *Persea americana* biodiesel yield and its blends on direct injection, compression ignition engines. Data Brief 21, 1533–1540.
- Anawe, P.A.L., Folayan, J.A., 2018b. Novel synthetic based drilling fluid through enzymatic inter-esterification of canola oil. Int. J. Chem. Eng. Article ID 6418090. Hindawi.
- Anawe, P.A.L., Folayan, J.A., 2018c. Data on optimization of production parameters on *Persea americana* (avocado) plant oil biodiesel yield and quality. Data Brief 20, 855–863.
- AOAC, 1990. Official Methods of Analysis, fifteenth ed. Association of official analytical chemists. AOAC pub., Virginia, Usa, pp. 69–84, 951–979.
- Azam, M.M., Waris, A., Nahar, N.M., 2005. Prospects and potential of fatty acid methyl esters of some non-tradition seed oils for use as biodiesel in India. Biomass Bioenergy 29 (4), 293–302.
- Bangboye, A.I., Hansen, A.C., 2008. Prediction of cetane number of biodiesel fuel from the fatty acid methyl ester (FAME) composition. Int. Agrophysics 22 (1), 21–29.
- Bari, S., Yu, C.W., Lim, T.H., 2002. Performance deterioration and durability issues while running a diesel engine with crude palm oil. Proc. Inst. Mech. Eng. D 216, 785–792.
- Bello, E.I., Adekanbi, I.I., Akinbode, F.O., 2015. Production and characterization of coconut (*Cocos nucifera*) oil and its methyl ester. Eur. J. Eng. Technol. 3 (3), 25–35.
- Cherng, Y.L., Lin, Yi-wei., 2012. Fuel characteristics of biodiesel produced from a high acid oil of soyabean soap stock by supercritical-methanol transesterification. Energies 5 (2012), 2370–2380.
- Demirbas, A., 1997. Calculation of higher heating values of biomass fuels. Fuel 76 (5), 431-434.
- Demirbas, A., 1998. Fuel properties and calculation of higher heating values of vegetable oils. Fuel 77 (9–10), 1117–1120.
- Demirbas, A., 2008. Biodiesel: A Realistic Fuel Alternative for Diesel Engine. Springer-Verlag London, Limited.
- Dunn, R.O., Knothe, G., 2001. Alternative diesel fuels from vegetable oils and animal fats. J. Oleo Sci. 50 (5), 415–426.
- Durret, T.P., Benning, C., Ohirogge, J., 2003. Plant triacylglycerols as feed stocks for the production of biofuels. Plant J. 54 (4), 593–607.
- Echim, C., Maes, j., Greyt, W.D., 2012. Improvement of cold flow filter plugging point of biodiesel from alternative feed stock. Fuel 93 (2012), 642–648.

- Encinar, J.M., Gonzalez, J.F., Rodriguez-Reinares, A., 2007. Ethanolysis of used frying oil biodiesel preparation and characterization. Fuel Process. Technol. 88 (5), 513–522.
- European committee for standardization, 2003. Committee for Standardization of Automotive Fuels-Fatty Acid FAME for Diesel Engines Requirements and Test Methods. European committee for standardization, Brussels, EN, 14214. Gaurav, D., Verma, P., Sharma, M.P., 2016. Impact of oil and biodiesel on engine
- operation in cold climatic condition. J. Mater. Environ. Sci. 7 (12), 4540–4555. Gentechscientific.com, 2018. Gas Chromatography. http://gentechscientific.com/
- gas chromatography. (Accessed 5TH August 2018).
  Hoekman, S.K., Broch, A., Robbins, C., Cenicerous, E., Nataraj, M., 2012. Review of biodiesel composition properties and specifications. Renew. Sustain. Energy Rev. 16, 143–169.
- kalayasiri, P., Jayashoke, N., Krisnangkura, K., 1996. Survey of seed oils for use as diesel fuels. J. Am. Oil Chem. Soc. 73 (4), 471–474.
- Khalid, k., Musa, M., Jusoff, K., Abdullah, R., Madina, Z., Zaini, M.D., Samsudin, A., 2011. Lowering of palm oil cloud point by enzymatic acidolysis. World Appl. Sci. J. 12, 28–31.
- Klopfenstein, W.E., 1985. Effect of molecular weights of fatty acid esters on cetane numbers as diesel fuels. J. Am. Oil Chem. Soc. 62 (6), 1029–1031.
- Knothe, G., 2005a. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Process. Technol. 86 (2005), 1059–1070.
- Knothe, G., 2005b. Viscosity of biodiesel. In: The Biodiesel Handbook. Chapter 6.2. AOCS press, Champaign, II, USA.
- Knothe, G., Bagby, M.O., Ryan, T.W., 1998. Precombustion of fatty acids and esters of biodiesel: A possible explanation for differing cetane numbers. J. Am. Oil Chem. Soc. 75 (1998), 1007–1013.
- knothe, G., Dunn, R.O., Bagby, M.O., 1997. Biodiesel: the use of vegetable oils and their derivatives as alternative diesel fuels. In: Fuels and Chemical Biomass, first ed. American Chemical Society, New York.
- Knothe, G., Dunn, R.O., Gunstone, F.D., Hamilton, R.J., 2001. Oleochemical Manufacturing and Applications. Sheffield Academic Press, Sheffield, UK, p. 106.
- Knothe, G., Matheaus, A.C., Ryan, T.W., 2003. Fuel 82 (2003), 971.
- Knothe, G., Steidley, K.R, 2005b. Kinematic viscosity of biodiesel fuel components and related compounds: influence of compound structure and comparison to petrodiesel fuel components. Fuel 84 (9), 1059–1065.
- Knothe, G., Van-Gerpen, G., Krahl, J., 2005a. The Biodiesel Hand Book. AOCS Press, Urbana, Illinois, pp. 278–280, Table, A-1, Properties of Fatty Acids and Esters of Relevance to Biodiesel.
- Krisnangkura, K., 1986. A simple method for estimation of cetane index of vegetable oil methyl esters. J. Am. Oil Chem. Soc. 63 (4), 552–553.
- Lamaisiri, C., Punsuvon, V., Chanprame, S., Arunyanark, A., Srinives, P., Liangsakul, 2015. Relationship between fatty acid composition and biodiesel quality for nine commercial palm oils, Songklanakarin. J. Sci. Technol. 37 (4), 389–395.
- Lee, I., Johnson, L.A., Hammond, E.G., 1995. Use of branched-chain esters to reduce the crystallization temperature of biodiesel. J. Am. Oil Chem. Soc. 72 (10), 1155–1160.
- Mohammed, A., Mohammad, G.S., Nanjappa, A., Rahman, M.M., 2018. Optimization of second-generation biodiesel production from Australian native stone fruit oil using response surface method. Energies 11 (2018), 2566.

- Mohibbe, A., Amtul, W., Nahar, N.M., 2005. Prospect and potential of fatty acid methyl esters of some non-traditional seeds oil for use as biodiesel in India. Biomass Bioenergy 29 (2005), 293–302.
- Nadia, S., Jumat, S., Emad, Y., 2013. The effect of chemical structure on pour point, oxidative stability and tribological properties of oleic acid trimester derivatives. Malays. J. Anal. Sci. 17 (1), 119–128.
- Rafaat, A.A., 2009. Correlation between the chemical structure of biodiesel and its physical properties. Int. J. Env. Sci. Technol. 6 (4), 677–694.
- Rashid, U., Anwar, F., Moser, B.R., Samia, A., 2008. Production of sunflower methyl esters by optimized alkali-catalyzed methanolysis. Biomass Bioenergy 32 (12), 1202–1205.
- Salles, K., Meneghetti, S.M.P., Ferreira de la, S.W., Meneghetti, M.R., dos santos, L.C.F., da silva, J.P.V., de Carvalho, S.H.V., Soletti, J.I., 2010. Characterization of Syagrus coronate (Mart) Becc. Oil and properties of methyl esters for use as biodiesel. Ind. Crop. Prod. 32, 518–521.
- Silitonga, A.S., Atabani, A.E., Mahlia, T.M.I., Masjuki, H.H., Badruddin, I.A., Mekhilef, S., 2011. A review on prospect of *Jatropha curcas* for biodiesel production in Indonesia. Renew. Sustain. Energy Rev. 15 (8), 3733–3756.
- Silitonga, A.S., Mahlia, T.M.I., Kusumo, F., Dharma, S., Sebayang, A.H., Sembiring, R.W., Shamsuddin, A.H., 2019. Intensification of Reutealis Trisperma Biodiesel Production using Infra-Red Radiation: Simulation, Optimization and Validation.
- Silitonga, A.S., Masjuki, H.H., OngHwai, C., Yusuf, T., Kusumo, F., Mahlia, T.M.I., 2016. Synthesis and optimization of *Hevea brasiliensis* and *Ricinus communis* as feed stock for biodiesel production: A comparative study. Ind. Crop. Prod. 85 (2016), 274–286.
- Smith, P.C., Ngothai Y. Nguyen, Q.D., O'Neill, B.K., Improving the low temperature properties of biodiesel: methods and consequences Renew. Energy, 35 (6) 1145–1151.
- Stephen, J.R., Naoko, E., 2013. Use of isomerization and hydroisomerization reactions to improve the cold flow properties of vegetable oil based biodiesel. Energies 2013 (6), 619–633.
- Tomasevic, A.V., Siler-marinkovic, S.S., 2003. Methanolysis of used frying oil. Fuel Process. Technol. 81, 1–6.
- Uriate, F.A., 2010. Biofuels from Plant Oils: A Book for Practitioners and Professionals Involved in Biofuels, to Promote a Better and more Accurate Understanding of the Nature, Production and Use of Biofuels from Plant Oils. National Academy of Science and Technology. Government of Japan. Japan ASEAN Solidarity Fund.
- Van-gerpen, j., Shanks, B., Pruszko, R., Clements, D., Knothe, G., 2004a. Biodiesel Analytical Methods. National renewable energy laboratory, NRRL/SR-510-362440.
- Van-gerpen, j., Shanks, B., Pruszko, R., Clements, D., Knothe, G., 2004b. Biodiesel production technology. National renewable energy laboratory, NRRL/SR-510-36244.
- Verissimo, M.I.S., Teresa, M., Gomes, S.R., 2011. Assessment on the use of biodiesel in cold weather: pour point determination using a piezo-electric quartz crystal. Fuel 90 (6), 2315–2320.
- Verma, P., M.P., Sharma, Gaurav, D., 2016. Evaluation and enhancement of cold flow properties of palm oil and its biodiesel. Energy Rep. 2 (2016), 8–13.
- Zhou, W., Konar, S.K., Boocock, D.G.B., 2003. Ethyl esters from the single-phase base-catalyzed ethanolysis of vegetable oils. J. Am. Oil Chem. Soc. 80 (4), 367–371.