Multidisciplinary Journal of Natural and Applied Sciences
Volume 13 Issue 3, July-September 2025
ISSN:2995-4142
Impact Factor: 10.52
https://kloverjournals.org/index.php/sciences

THE INFLUENCE OF CARBON CHAIN LENGTH AND UNSATURATION ON PHYSIOCHEMICAL PROPERTIES OF BIODIESEL

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DOI: https://doi.org/10.5281/zenodo.16994193

Abstract: The impact of oil classification on various physical and chemical properties of biodiesel were studied. Five vegetable oils with varying numbers of carbon chain, degree of saturated and unsaturated fatty acids was used. The vegetable oils were transesterified using sodium hydroxide as catalyst employing standard reaction conditions. This study revealed that some physical (specific gravity, kinematic viscosity, and cloud point) and chemical (acid value, iodine value, and peroxide value) properties of the biodiesel produced increases alongside increase in carbon chain length and degree of unsaturation. The longer saturated carbon chain (groundnut oil) and higher degree of unsaturation (soybean oil) the higher specific gravity, kinematic viscosity, cloud point, acid value, iodine value, and peroxide value of the biodiesel than those produced from shorter saturated carbon chain fatty acid (palm kernel oil, and palm oil) and lower degree of unsaturation (olive oil). These biodiesels will not biologically degrade and is within ASTM common standards and suitable for use as biodiesel with significantly less environmental concerns.

Keywords: Carbon chain length, unsaturation, Biodiesel, Physicochemical properties, ASTM specification standard.

Introduction

Vegetable oils and animal fats are source of energy that cannot be used as engine fuel and to overcome the problem associated with the direct use, a transesterification reaction of oils or fats and an alcohol to produce a mixture of mono-alkyl esters of long-chain fatty acids fuel with properties more similar to petroleum diesel, making it suitable for use in diesel engines are produced (Umeh & Okonkwo, 2025; Vilas Bôas & Mendes, 2022; Elgharbawy et al., 2021; Ejikeme et al., 2013; Ikechukwu et al., 2021; Ramachandran et al., 2013).

Vegetable oils and animal fats consist predominantly of glycerol esters of fatty acids that are insoluble in water and belong to a class of lipids known as simple lipids that can be saponified with KOH and NaOH. Most vegetable oils are mixed triglyceride as more than one kind of fatty acid may be present and in varying quantities with two or three predominating. The type and concentration of fatty acid present determines the properties of a vegetable oil. Generally vegetable oils are composed of 18 carbon chain fatty acids with different degree of unsaturation. The three carboxylic acids attached may be the same and termed tristearin but if different are called mixed acids (Ahmed et al., 2023; Kerr et al., 2015; Berg et al., 2012).

Natural oils and fats are classified generally according to their origin as vegetable, animal or marine oil. Of these, vegetable oil is the most important and the world production stood at 228 million metric tons for the year 2024/2025 being more than double the combined production from animals and marine sources (Shahbandeh, M. 2025; Nieto & Lorenzo, 2022; Maqsood-ul-Haque & Veny, 2023; Adeoye, 2022; Sharma et al., 2022).

Structurally fixed oils (so called because they are not volatile and cannot evaporate) are classified according to their ability to absorb atmospheric oxygen due to kind of fatty acids combining with glycerol resulting in diverse types of oils., namely non-drying oils, semi-drying oils, and drying oils (Sharma et al., 2022; Daga et al., 2022; Kodali, 2014).

Nondrying oils are those that do not contain any double bond that can react (form oleochemical polymers) with atmospheric oxygen to cause any appreciable drying (solid film). It constitutes largely of oleic acid glycerides and the iodine values are below 100. The fatty acids commonly found in non-drying oils are palmitic, stearic (saturated fatty acid). They are mainly used in the manufacture of soaps, as lubricants, and are used in food, e.g., groundnut, palm, olive, castor, rape seed and almond oil. Non-drying oils are considered very good for biodiesel production because they do not form solid film when exposed to air, are readily available and relatively inexpensive, biodegradable and have low sulfur and aromatic content and will not constitute any environmental challenges when burned (Silvaet al., 2021; Karmakar et al., 2020; Sirigeri et al., 2019; Kanwar Rawat et al., 2021; Gunstone, 2011).

Semi-drying oils are intermediate between the non-drying and drying oils and are known to have a large amount of two double bonds linoleic and saturated acids but no linolenic acid. They react slowly with atmospheric oxygen producing only a soft film after extended exposure. The iodine number is between 100 and 140. Included in this class are cotton seed, sesame, sunflower, corn, soybean, rapeseed oils. They are generally good for biodiesel production because they possess an intermediate unsaturation and are readily available (Islam et al., 2014; Tumosa & Mecklenburg, 2003; Sarah Sands, 2011: Keat, 2022: Stenberg, 2004: N. Jones & Peter Pappas, 2017).

Drying oils are rich in glycerides of the ***polyunsaturated fatty acids*** (must contain at least 50% polyunsaturated fatty acid) particularly linoleic and linolenic with few oleic compounds. They readily react with atmospheric oxygen on exposure to air and form a tough, elastic but resistant film, drying oils have a high iodine number, generally more than 130. They are predominant in temperate plants like Linseed, safflower, soyabean etc (N. Jones & Peter Pappas, 2017; Maliki et al., 2020; Encyclopaedia

Britannica, 2025; Rahim et al., 2023; Poth, 2001; Eromosele & Eromosele, 2002). Due to high iodine number and attendant oxidative potentials, most drying oil need prior treatment.

Semi-drying oil are considered first among non-drying and drying oils owing to the fact that most of the seed bearing them are cultivated in large scale, contain high oil content, most appropriate for transesterification, with minimal pretreatment and post- treatment, and more so emphasis is on the use of non-edible oil so as not to compete with food crops (Umeh & Okonkwo, 2025; Vilas Bôas & Mendes, 2022; Shikha & Rita, 2012).

To enhance transesterification, and produce high-grade biodiesel involves careful selection of pure oil, working at the optimal temperature range of 55-65°C, acid or base catalyst (NaOH, KOH, calcium oxide, etc. and HCl and H_2SO_4) concentration of 1-5 % and alcohol (methanol or ethanol) -to-oil ratio. Methanol is preferred due to the short carbon chain, and the high **ability to store electrical energy (dielectric constant)** that enhances transesterification reactions, particularly those involving polar interactions and ionic (NaOH) species in polar solvents (Mumtaz et al., 2017; Sajjad et al., 2022; Kedir et al., 2023; Onukwuli, et al., 2017; Ao et al., 2024; Haider et al., 2021; Changmai et al., 2020; Murthya & Kumar, 2021; Zik et al., 2020; Mamuye & Ali Shemsedin Reshad, 2022; Anisah et ., 2019; Liu et al., 2019; Antunes et al., 2008).

Material and method

Reagents

Commercial groundnut oil, olive oil, palm oil, soybean oil, and palm kernel oil; methanol, NaOH

Sample collection/preparation

The oil samples used are groundnut oil, olive oil, palm oil, soybean oil, and palm kernel oil were bought from Ogbete Main Market, Enugu. The palm oil was heat bleached to remove the pigments at 255°C. Methanol and NaOH were of analytical grade.

Method of transesterification reaction

Sodium hydroxide (7.5 g) was dissolved in 200 ml methanol by stirring vigorously till fully dissolved. The oil (1000 ml) was measured and heated to 60°C in a stainless container, then the solution of sodium hydroxide in methanol added and heated in a closed system (pressure pot) in a water-bath at the temperature of 60°C for 4 hrs. with care to avoid explosion. Finally, the prepared mixture was poured into a separating funnel phase separation and allowed without disturbance for 4 hrs. Out of the two layers observed, the upper layer (crude biodiesel) was light yellowish in colour while the lower layer composed of glycerol and catalyst was brownish.

Separation and purification of biodiesel

The crude biodiesel was separated and washed severally with a lot of distilled water to remove any soap molecule formed by side reaction till no foam was formed. Then air was bubbled through a pressure pump for 20 minutes to remove volatile gases formed with the biodiesel. Finally residual water was removed from the biodiesel produced by heating it in an electric oven at 105°C for two hrs.

Physical properties of biodiesel

Specific gravity determination

Specific gravity bottle method was employed where the weight of a specific volume of the biodiesel produced was divided by weight of equal volume of distilled water to obtain the specific gravity of the biodiesel.

Viscosity measurement

An Ostwald viscometer method was employed in this viscosity determination. The Ostwald viscometer was clamped on a retort stand dipping inside a water bath at 40°C and the biodiesel into it and sucked up into the upper bulb and allowed to fall freely. A stop-watch was started and the time taken for the biodiesel to fall between the upper graduation mark and the lower graduation mark was read and recorded.

Pour point determination

The produced biodiesel was collected with a tiny capillary tube and freeze in a freezer. Afterwards, the capillary tube was removed and placed in a watch glass used to cover a beaker of water heated slowly. A thermometer was inserted I the water bath. The lowest temperature at which the biodiesel can flow when it is cooled was read and recorded as is known as the pour point.

Cloud point determination

In this determination, a capillary tube was used to collect the produced biodiesel and placed on flat glass sheet and used to cover a trough filled with ice chips. Then a thermometer was dipped to be touching the glass sheet. The temperature at which the biodiesel turned cloudy was recorded as the cloud point of the biodiesel produced.

Moisture content determination

Five grams of the produced biodiesel was weighed into an evaporating dish and placed in a drying oven at 105°C for two hours and weighed. Then the biodiesel was weighed at an interval of 30 minutes till a constant weight was attained. The constant weight of the biodiesel was subtracted from the initial weight and used to calculate the percent moisture content.

Chemical properties of biodiesel

Acid value determination

A mixture of 25ml diethyl ether and 25ml of ethanol was used to dissolve 2g of the biodiesel. The solution was titrated with 0.1M NaOH using phenolphthalein as indicator to a faint pink colour that persisted for 15 seconds. Acid value = %FFA (as Oleic) × 1.99

Determination of saponification value

Alcoholic potassium hydroxide solution (0.5 M) 25ml was used to hydrolyze (reflux) 2g of biodiesel produced for 1 h with frequent agitation. The unreacted alkali after the hydrolysis was titrated with 0.5 M hydrochloric acid using 1 mL of phenolphthalein as indicator. A Blank titration was carried out alongside and the Saponification value calculated thus:

$$\text{Saponification value} = \frac{(\text{Blank} - \text{Titre value}) \times 28.05}{\text{Weight of oil (g)}}$$

Determination of iodine value

One gram of the produced biodiesel was reacted with 25ml of Wijs reagent in a stoppered flask kept alongside a blank where 10ml of chloroform instead of biodiesel were kept in the dark for 2 hrs. after

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Volume 13 Issue 3, July-September 2025
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shaking very well. After the 2 hrs. the stopper was removed and rinsed with 50ml of distilled water into the mixture respectively, 10ml of 10% KI solution was then added. The liberated iodine in biodiesel and blank was titrated with a standardized sodium thiosulfate solution (0.1M), using starch as an indicator respectively. The titration was continued from brownish yellow to blue colour that disappears at the end point is attained.

Formula for calculating iodine value:

Iodine Value = (B - S) × N × 12.69 / W

Where:

(B - S) = difference in mL of sodium thiosulfate used for the blank minus that used for biodiesel

M = molarities of the sodium thiosulfate solution used.

12.69 = conversion factor (g I2 / mEq $Na_2S_2O_3$).

W = weight of the biodiesel sample in grams.

Peroxide value determination

One gram of the produced biodiesel was boiled in a clean dry boiling tube with 1g KI and 20ml of mixed solvent (glacial acetic acid 12: chloroform 1) in a boiling water bath for 1 minute, and poured into 25ml of 5% KI. The boiling tube was washed twice with 25ml distilled water and the wash water added and titrated with 0.002M sodium thiosulphate using starch indicator. A blank was similarly treated and titrated.

Peroxide value (meq/kg) = $\frac{1000(V2-V1)T}{M}$

Where:

M = mass of oil taken (1 g);

V2 = volume of 0.1 N $Na_2S_2O_3$ used for biodiesel

V1 = volume of 0.1 N Na2S2O3 used for blank

T = normality of Na2s2O3 (0.1 N)

Results and discussion

In order to x-ray the influence of carbon chain length in biodiesel, it is of great importance to have a good knowledge of its physical and chemical characteristics. This had been quite accomplished in this study and the results represented in Table 1.

Table 1. The results of the physicals and chemical properties of the biodiesels produced

Parameters	**Biodiesel sample**				
Physical properties	**Palm kernel oil (14:0)**	**Palm oil (16:0)**	**Olive oil (18:1)**	**Soybean oil (18:2)**	**Groundnut oil (20:0)**
Specific gravity	0.872	0.877	0.876	0.882	0.885
Kinematic viscosity (mm^2/s at 40(°C))	5.3	5.5	5.6	5.8	5.9
Cloud point (°C)	14.0	15.2	14.4	15,5	15.8

Pour point (°C)	11.9	16.2	14.3	4.7	7.8
Moisture content (%)	0.02	0.04	0.01	0.02	0.03
Chemical properties					
Acid value (mg KOH/g)	0.28	0.39	0.32	0.37	0.44
Saponification value (mg KOH/g)	226	197	189	187	191
Iodine value (g I2/100 g)	37.11	53	88	122	84
Peroxide value (meq/kg)	5.9	6.1	4.4	5.6	6.7

Key: Figure in parenthesis represents carbon chain number and degree of unsaturation

The results of the specific gravity determination in this study revealed that biodiesel of saturated oils (palm kernel (14), palm oil (16), and groundnut oil (20)) probably increases as carbon atom increases. Also, the specific gravity of biodiesel of unsaturated oil was found probably to increase with increase in degree of unsaturation (olive oil 18 :1, and soybean 18: 2). However, this study revealed that specific gravity of biodiesel produced are higher than the specific gravity of petroleum (fossil) diesel (0.85) by ASTM standard but varies within the range (0.86 and 0.90) specific gravity of biodiesel (Dunford, 2016, Tesfa et al., 2010; Tat & Van Gerpen, 2000; Onimisi et al., 2021).

From the result obtained (Table 1), the Kinematic viscosity (mm^2/s at 40(°C) of the formulated biodiesels increases with increase in carbon chain length of saturated oil while the Kinematic viscosity decreases as the degree of unsaturation increases. All the biodiesel formulated in this study are all viscus but is still with the agreed Kinematic viscosity (mm^2/s at 40(°C) standard of 1.9–6.0 mm^2/s in the American standard ASTM D6751 (Knothe, G. & Steidley, K.R. (2007).

The cloud point obtained in this study shows that the cloud point increases with increase in carbon chain length of saturation and degree of unsaturation of fatty acid esters. It is observed (Table 1) that only palm kernel oil and olive oil biodiesels that are within the standard ideal cloud point range of — 3°C and 15°C, while the cloud points of palm oil, soybean oil and groundnut oil biodiesels are slightly above the recommended range. This could probably be due to practical performer error (Kumbhar et al., 2022; Folayan et al., 2019; Refaat, 2009).

Generally, the pour point gives idea about the temperature below which a liquid can not flow and ironically this study revealed that the pour point of the biodiesels produced varies probably due to some factors such as the quantities of saturated fatty acids, degree of unsaturation, length of carbon chain and nature of branching. It is only palm oil biodiesel that have pour point slightly above specified limit of – 15 to 16°C as reported in ASTM D6751, while biodiesels of palm kernel, olive, soybean, and groundnut oils are within the specified limit (Reddy et al., 2018).

The moisture content of the biodiesel produced as determined were all found to be within the specific limit 0.05% moisture content (Umeh & Okonkwo, 2025). The biodiesels so produced will not degraded due to microbial attack, and will not collude the fuel system.

It is clearly from the findings of this study that fatty acid increases with in carbon chain length and degree of unsaturation respectively. The results of fatty acid determination are in agreement with the

limit specified in standards like ASTM D6751 and EN14214 for pure biodiesel the acid value should be lower than 0.5 mg KOH/g. Higher content can lead to several consequences such as colluding of the fuel system, and deposit accumulation of fatty acids that probably reduced fuel quality (Folayan et al., 2019; Islam et al., 2013; Shalaby, 2013).

The palm kernel oil biodiesel was found to have saponification value much higher than the specified limit probably due to its low molecular weight and shorter carbon chain length. This indicates higher tendency to form soap and consume the alkali (NaOH) catalyst than others that have their saponification values within the specified limit range of 188 to 207 mg KOH/g and reduce yield. Biodiesel of palm kernel oil will need more extensive washing to remove the soap formed than others. From the trend of the result, it was observed that saponification value decrease with increase in carbon chain length and degree of unsaturation (Umeh & Okonkwo, 2025; Bong et al., 2020; Bello et al., 2015; Olatundun et al., 2024; Mekonnen et al., 2024; Knothe, 2016; Primata et al., 2013).

Iodine values of the biodiesels were observed to increase with increase in degree of unsaturation and also with increase in carbon chain length probably because the oils are composed of mixed fatty acids. However, it is only the iodine value for soybean oil biodiesel that was higher than the maximum recommended limit of 120 g I2/100g according to the EN 14214 standard and ASTM D6751 due to interaction with environmental oxygen and probably responsible for the high viscosity which mighty affect engine performance (Umeh & Okonkwo, 2025; Adeyemi et al., 2021; Osarumwense et al., 2020).

The peroxide value of the produced biodiesel ranged from 4.4-6.7 (meq/kg), all below the maximum limit (10 meq/kg) for biodiesel, indicating stability against oxidation and not likely to go rancid. Olive oil biodiesel had the least value while groundnut oil biodiesel had the highest value. However, it was observed that peroxide value increases with increase in carbon chain length and degree of unsaturation (Ismail & Ali, 2015; Orhevba et al., 2016; Oduche et al., 2025).

Conclusion

The vegetable oils used in synthesis of biodiesel effect some of the physical and chemical properties of biodiesel. Biodiesel produced from a longer carbon chain and high degree of unsaturation tend to have higher physical (specific gravity, kinematic viscosity, and cloud point) and chemical (acid value, iodine value, and peroxide value) properties than biodiesel produced with shorter carbon chain and lower degree of unsaturation. It can therefore be concluded that oils with shorter carbon chain number and lower degree of unsaturation are better for producing high quality biodiesel than oil of longer carbon chain length and higher degree of unsaturation.

Conflict of interests

The author(s) did not declare any conflict of interest.

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