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This research tested the hypothesis of whether fatty acid saturation and chain length of feedstock oil has any effect on the physicochemical properties of synthesized kerosene-like fuel. Biodiesel was obtained from the feedstocks via transesterification and were subjected to distillation under vacuum between 50 to 100 °C to obtain kerosene-like fuel as the final product. The heat value, flash points, kinematic viscosity and specific gravity values were obtained and found to be within the stipulated range of fossil kerosene. The products were analysed using infrared spectrometer to confirm the presence of the functional groups in the kerosene-like fuel produced. Furthermore, Analysis by the elemental analyser showed that the kerosene-like fuel obtained from coconut oil has a significantly higher heat content value (9211.9 Kcal.Kg⁻¹) than that from cashew-nut oil (5699.4 Kcal.Kg⁻¹). This distinction in heat value can be ascribed to the nature of fatty acid in the oils as coconut oil is significantly more saturated and has shorter fatty acid hydrocarbon chain length than cashew-nut oil.

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Introduction

For many years, crude oil has been the major source of energy worldwide. The call for a sustainable alternative can be ascribed to many factors. Amongst these factors are that it is non-renewable, the ever increasing demand and the environmental impacts. In developing countries especially in sub-Sahara Africa, kerosene is in high demand for domestic cooking but scarcity and rising costs have not helped the situation. Kerosene and jet fuel price fluctuations due to social and political instability in the countries where the oil reserves are located have prompted many countries to find alternatives1 and it is envisaged that the use of renewable and efficient fuel will be the solution to these problems. In terms of environmental impact, aircrafts emissions onground and in-flight have raised some concerns. Emissions of pollutants such as carbon dioxide, carbon monoxide, hydrocarbons, sulfur oxides, sulfates, and airborne particles have well been documented.

Various approaches have been conducted by many authors to produce biofuel e.g., Fischer-Tropsch (FT).²⁻⁴ and other methods.⁵⁻⁷ Hydrotreatment and isomerization of vegetable oil is another option. In this process, oxygen atoms were removed and C=C bonds are saturated by hydrogen.⁴ The synthesis and use of fatty acid methyl esters (FAME) as kerosene-like fuel is another option.⁸⁻¹¹ In general, kerosenelike fuel which constitutes the lower molecular weight fraction of FAME can be obtained from FAME by distillation under vacuum. Production of biodiesel from different sources via transesterification have been reported; sources such as chicken fat,¹² castor seed oil,¹³ dairy waste scum,¹⁴ and vegetable oil,^{15,16} have been used successfully to produce biodiesel. Vegetable oils are viable sources of renewable fuel,¹⁷⁻²⁵ the biofuel produced is cleaner with less greenhouse gases emission.²⁴

Vegetable oils are transesterified with methanol to produce biofuel, and then subjected to fractional distillation under vacuum. It possesses high level of lubricity and detergency which make it possible to improve on the performance of fossil kerosene and contribute to the cleaning of the turbine. Although, American Society for Testing and Materials (ASTM) has not approved FAME as a jet-fuel blend, it specifies 5 mg kg⁻¹ as the maximum allowable level in jet fuel as the functional definition of "nil addition".27 However, other alternatives have a common drawback. Unlike FAME, they do not have any oxygen in their molecular structures. The presence of oxygen in a fuel has two main advantages; there is a reduction of carbon content in the fuel, thus, soot formation (emission) of the fuel is significantly reduced,^{28,29} and secondly, aircraft's engine particulate matter emissions fall by almost 40 % when jet fuel was blended with oxygenated fuels.³⁰

A lot more effort in research is still needed in this field. Knowledge of the chemical composition of oil and especially the fatty acid composition in the triglyceride in oil will be a good guide in selecting feedstock for FAME production. Some of the key things to take into consideration are the number of chain length and level of saturation of fatty acid in oil; these factors can play key roles in the properties of the formed FAME such as heating value. In this work, kerosene-like fuel was obtained through distillation under vacuum, at a temperature between 50 to 100 °C. Biodiesel was produced via base catalyzed transesterification of coconut and cashew nut oils. The effects of degree of saturation and chain length of fatty acid were studied and also the quality of the synthesized biofuel was verified using several tests and techniques such as heating value, flash point, kinematic viscosity, IR spectroscopy and GC-MS.

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Experimental

Chemicals and materials

High quality analytical grade reagents were used throughout the process and were not purified further. Threeneck round bottom flask (500 mL), condenser, and thermometer were of Fisher Brand. Potassium hydroxide and methanol were obtained from Breckland scientific supplies.

Synthesis of biodiesel from feedstock by transesterification

A 200 mL of Coconut oil or Cashew-nut oil were transferred into a 3-neck round bottom flask, a magnetic stirrer was placed into the flasks and the unit pre-heated to a temperature of 65 °C. To obtain potassium methoxide solution, 1.73 g of potassium hydroxide and 30 mL of methanol were mixed together in a flask. Furthermore, the solution was stirred to have a clear soluble solution and then added to the preheated oil. Reflux condenser was used to recycle the methanol to avoid evaporation of any excess methanol above 65 °C. The reaction was carried out for 60 min with constant stirring and the temperature was maintained at 75 °C throughout the process. After 60 min, the oil was transferred into a separating funnel and left over night for the separation of glycerol (lower layer) from biodiesel (upper layer).

Biodiesel was then purified by addition (with swirling) of 20 mL of warm distilled water in order to remove soap, unreacted methanol and potassium hydroxide in the biodiesel and then the mixture was allowed to stand to separate into two distinct layer. The washing process was repeated four times with different portions of 20 mL of water. Finally, the biofuel (biodiesel) was drained into a clean beaker and heated on a hot plate to remove moisture in the biofuel.

Production of kerosene-like fuel from bio-diesel

A 100 mL of coconut or cashew-nut biodiesel was poured respectively into a round bottom flask fitted to a Fisher vacuum distillation apparatus. The distillates were collected under vacuum from 50 to $100 \, {}^{0}$ C. The yield of kerosene-like fuel obtained from the biodiesel produced was 74.0 % (coconut oil) and 66.0 % (cashew nut oil) respectively.

Kerosene-like fuel analysis

Kinematic viscosities of the kerosene-like fuels were obtained by the use of 3C viscometer. 15 mL of each sample of the kerosene-like fuel was used to obtain the viscosities at 40 °C.

The energy content was obtained by the use of Flash 2000 series CHNSO elemental Analyzer. The flash analyzer was used to obtain gross heat value and the net heat value of the coconut and cashew-nut kerosene-like fuel produced by injecting the sample directly into the instrument by the use of an auto-sampler equipped with the instrument.

Kerosene-like fuel analysis

Nicolet IR 100 FT-IR machine was used for the purpose of providing insights regarding the functional groups of the products by using two drops of the kerosene-like fuel on a KBr salt plate to obtain the functional groups present. Tag closed cup flash point tester was used to analyzed coconut and cashew-nut kerosene-like fuel.

GC-MS was used to determine the chemical composition of the kerosene-like fuel produced from coconut and cashew nut oil. Agilent gas chromatography 7890A coupled with inert mass spectrometry detector 5975 C (MSD) was utilized. The injection technique was split-less mode coupled with an auto-sampler type, and injection volume of 1.0 µL. Furthermore, other conditions of the measurement include an oven temperature of 70 °C (hold for 1 min) with a programming rate 10 °C min⁻¹ to 280 °C, at 3 mins hold. For the MS detector, scanning range was full range scan of 50-550 amu at normal speed. An NBS75K.L mass spectral library was used to identify the components present in the samples. The chemical compositions of the kerosene-like fuel were detected as the displayed peaks of the chromatogram and the results from data base. The molecular weights of the components were calculated from the result of the composition from the mass spectra.

Results and Discussion

Fatty acid composition in oil

Table 1 shows the percentage fatty acid composition in coconut and cashew-nut oil.32-35 There is a significant difference in their relative chain length and degree of saturation. By comparing their relative chain length, they both have C18 as the longest chain length but percentage of C18 in coconut oil is approximately 9.06 % while that of cashew-nut is approximately 64.18 % For degree of saturation, cashew nut oil is significantly less saturated than coconut oil. Palmitoleic, oleic, linoleic and linolenic acid that contain unsaturated C-C bonds make up about 63.28% of cashew-nut oil fatty acid while oleic and linoleic acids containing unsaturated C-C bonds make up about 7.12% of coconut oil fatty acid. These key differences can be linked to the key properties of biofuel produced. For fossil fuels, the shorter and the more saturated the hydrocarbon chain, the higher the heat content tends to be.

 Table 1. Coconut and cashew-nut oil fatty acid composition.

Oil	Composition
Coconut	8:0 caprylic 6.21%, 10:0 capric 6.15%, 12:0 lauric 51.02%, 14:0 myristic 18.94%, 16:0 palmitic 8.62%, 18:0 stearic 1.94%, 18:1 oleic 5.84%, 18:2 linoleic 1.28%
Cashew	10:0 capric 1.37%, 12:0 lauric 1.83%, 14:0 myristic 0.59%, 16:0 palmitic 28.87%, 18:0 stearic 4.06%, 16:1 palmitoleic 3.16%, 18:1 oleic 34.48%, 18:2 linoleic 4.67%, 18:3 linolenic 20.97%

Properties of Kerosene and Kerosene-like fuels

Heating value

The heating value content for fuel is very important as the capacity to generate heat as a fuel is of utmost importance. The heat values generated by kerosene-like fuel from cashew-nut oil and coconut oil respectively under the same set of conditions are presented in Table 2. The heating value for kerosene-like fuel from coconut oil (9211.9 kcal kg⁻¹) and is significantly higher than that from cashew-nut oil (5699.4 kcal kg⁻¹), and not far from that of kerosene (10695.3 kcal kg⁻¹). The standard higher calorific value for kerosene is 46200 kJ kg (11034.41 kcal kg⁻¹).³¹ The former observation corroborates the information in Table 1 for fossil fuels, the shorter and more saturated the hydrocarbon chain, the higher the heat content tends to be.

Table 2. Properties of kerosene and kerosene like fuel.

Sample	Yield (%)	SP	FP @ 28 °C	HV (kcal kg ⁻¹)	KV (mm ² s ⁻¹) @40 °C
kerosene coconut oil fuel	- 74	0.86 0.87	46 40	10695.3 9211.9	2.99 3.88
cashew- nut fuel	66	0.82	38	5699.4	4.16

SP = specific gravity; FP = Flash point; HV = Heat value; KV = Kinematic viscosity.

Coconut and cashew-nut kerosene-like fuel were blended with fossil kerosene in the proportion 20% (B20) by volume of kerosene. As illustrated in figure 1, The heating value of the blended fuel were found to increase as a result of the blending with fossil kerosene, which signifies that blending of the kerosene-like fuel improves the quality of the kerosene-like fuel and surprisingly better than the fossil kerosene from the chart below.

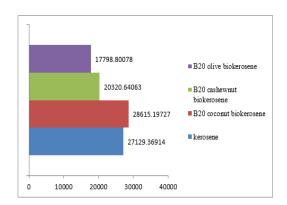
Properties of kerosene and kerosene-like fuel

Kinematic viscosity

Viscosity values indicate the degree of resistance of fluid to flow. As shown in table 2, the kinematic viscosity values at 40 ° C obtained for kerosene-like fuel from coconut and cashew-nut oil samples are 3.88 and 4.16 mm² s⁻¹ respectively. In comparison to kerosene (2.99 mm² s⁻¹), both biofuel products have higher values. However, both coconut and cashew-nut kerosene-like products met ASTM D1655 specification (<8 mm² s⁻¹) for Jet-fuel

Flash point analysis

Flash point values for fuels are very important because of the safety issue associated with it. The value obtained were 40 and 38 °C of coconut and cashew-nut kerosene-like fuel respectively. That of kerosene was also measured under the same condition as the kerosene-like fuels was obtained. These values indicate that these kerosene-like fuel products obtained meet the flash point safety condition.



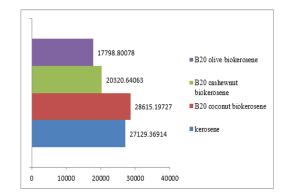


Figure 1. Heating value of (**a**) kerosene-like fuel and kerosene and (**b**) blend of kerosene like fuel and kerosene.

IR Spectroscopy

The IR spectra of kerosene-like fuel products obtained from both cashew and coconut oil showed typical strong C-H stretch and C-H bend as expected respectively at around 2900 and 1400 cm⁻¹. The C=O (from alkyl ester) stretch at around 1750 cm⁻¹. The C=C stretch (1650 - 1680 cm⁻¹), typically a weak or medium signal can be observed in the cashew-nut kerosene-like fuel spectrum but not found in the coconut kerosene-like fuel IR spectrum. This observation is not surprising because cashew-nut oil is relatively less saturated than coconut oil.

Gas chromatography mass spectrometry (GC-MS) analysis

The chemical compositions of the kerosene-like fuel were obtained from the chromatogram obtained in (Figure 2) and the results from data base. The molecular weights of the components were calculated from the result of the composition of the mass spectra.

The chromatogram of kerosene-like fuel produced from cashew-nut and coconut oil are shown in Figure 2 (a) and (b) respectively. These peaks represent the fatty acids that were converted to methyl esters (biofuel) as a result of the transesterification process. For cashew-nut kerosene-like fuel, the major methyl esters detected are octanoic acid [*caprylic*], methyl ester (6.87 min), nonanoic acid [*pelargonic*], methyl ester (8.35 min), decanoic acid [*capric*], methyl ester (9.86 min), dodecanoic acid [lauric], methyl ester (13.92 min), tetradecanoic acid [myristic], methyl ester (14.79 min), hexadecenoic acid [palmitic], methyl ester

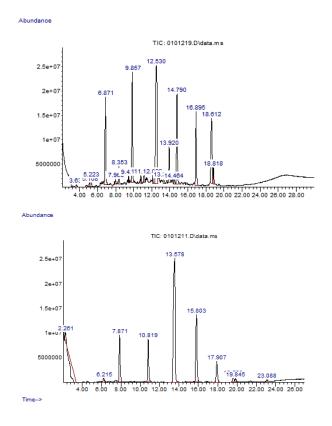


Figure 2. GC chromatogram of the kerosene-like fuel produced from (a) Cashew-nut oil (b) Coconut oil.

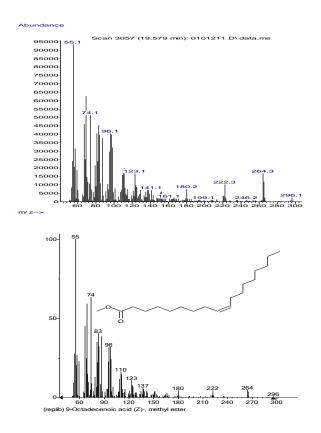


Figure 3a. MS of oleic acid methyl ester.

(16.89) and octadecenoic acid [oleic], methyl ester (18.60 min). While for coconut oil kerosene-like fuel, the major methyl esters detected are octanoic acid [*caprylic*], methyl ester (7.87 min), decanoic acid [*capric*], methyl ester (10.82

min), dodecanoic acid [lauric], methyl ester (13.58 min), tetradecanoic acid [myristic], methyl ester (15.80 min), hexadecanoic acid [palmitic], methyl ester (17.91 min) and octadecenoic acid [oleic], methyl ester (17.91 min).

The significant difference in the saturation levels of olive oil and cashew-nut oil biofuel was also reflected in methyl esters chromatograms; octadecenoic acid [oleic], methyl ester, the most prominent unsaturated fatty acid methyl ester in cashew-nut oil appeared in relative abundance of 1.5 x 10^7 while it appeared in coconut oil in relative abundance 1 x 10^5 . It is also worthy to note that GC-MS data confirmed the purity of these products; no peaks attributed to glycerol and methanol were detected.

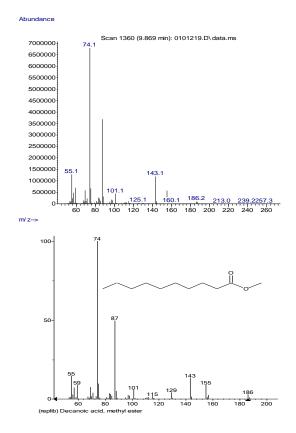


Figure 3b. MS of capric acid methyl ester of kerosene-like fuel produced from cashew nut oil

GC-MS analysis confirmed the formation of methyl esters of the expected fatty acids. Examples are shown in Figure 3, Figure 3(a) is that of oleic acid methyl ester while that of capric acid methyl ester is shown in figure 3(b).

Conclusion

Kerosene-like fuel was successfully synthesized from coconut and cashew-nut oil via alkaline based transesterification at 75 °C. Biodiesel products were obtained from the feedstocks via transesterification and then subjected to distillation under vacuum between 50 to 100 °C to obtain kerosene-like fuel as the final product with high yields of bio-kerosene; 74 % and 66 % for coconut and cashew nut kerosene-like fuel respectively.

This shows the closeness of the physico-chemical properties of the kerosene-like fuel to that for fossil kerosene. Kerosene-like fuel obtained from coconut oil has a significantly higher heat content value (9211.9 kcal kg⁻¹) than that obtained from cashew-nut oil (5699.4 kcal kg⁻¹). This can be ascribed to the nature of fatty acid in the oil; coconut oil is significantly more saturated and has shorter fatty acid hydrocarbon chain length than cashew-nut oil. For fossil fuels, the shorter and the more saturated the hydrocarbon chain, the higher the heat content. Gas chromatography-mass spectrometer (GC-MS) analysis of produced kerosene-like fuel confirmed the type of methyl esters that were expected to be in the kerosene-like fuel. In the future, possible use of their respective waste cooking oil as feeds to produce kerosene-like fuel will be looked into. and also taking into consideration the nature of the oil fatty acids.

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