Agricultural Science Research Journal
ISSN 2026-6073
Lawal and Olalekan, Volume (9) Issue (4): 35 – 41 June – 2019. RESEARCH PAPER

Physicochemical properties of *Citrullus lanatus* (Melon Seed) and *Cocos nucifera* (Coconut) Oil Blends and applications as cutting fluid

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Abstract

This research focused on the physicochemical properties of blended vegetable oils using *Citrullus lanatus* oil (melon seed oil-MSO) and *Cocos nucifera* oil (coconut oil-CNO) as the case study for use as cutting fluid in machining operations. In the investigation carried out on the oils, physical properties such as viscosity, flashpoint, specific gravity, density, pour point, cloud point and thermal stability were determined through a conducted laboratory experiment. The study also involved the determination of chemical properties like iodine value, acidic value, saponification value, hydrogen peroxide value and free fatty acid value according to each testing standards. The oils were blended at ratios 20:80, 40:60, 60:40 and 80:20 to obtain suitable blending ratios. Based on the analysis, the physicochemical properties of oil blend at 60%:40% provides a suitable results for use as a cutting fluid in machining operations with the following properties: acidic value (1.683mgNaOH/g), free acid value (0.842mgNaOH/g), specific gravity (41.467g), density (1.658g/mL), viscosity at 40 ^{0}C (22.50pa.s), viscosity at 120 ^{0}C (4.00pa.s), iodine value (139 mgKOH/g), pour point (–1^0), flash point (284 ^{0}C), saponification value (121 mgKOH/g), Hydrogen peroxide value (4.91 mgKOH/g) and cloud point (10 ^{0}C). The thermal stability of this ratio is also appreciable for cutting fluid. Based on the above results, the research shows that blended vegetable oils can be adapted as a suitable substitute for mineral oil in machining operations due to their improved qualities and functionalities.

Keywords: Seed, Coconut, Oil, blends, Physicochemical, Properties

Introduction

Modern lubricants are generally composed of more than 80% base oil and a smaller amount of functional additives (Arbain & Salimon, 2009). The merits caused by the mineral oil based stock have been questioned lately due to the several negative effects they have caused in the environment and workers' health (Norby, 2003). As a result, the base oil mainly determines lubricant properties such as oxidative stability, low-temperature flow properties and lubricity. There are three categories of base oils namely mineral oils, synthetic oils and vegetable oils.

Traditionally, over 85% of base oils are refined from crude petroleum (Yunus, *et al*., 2005).However, with the decreasing stocks of petroleum and high costs of synthetic lubricant, vegetable oils are considered to be potential candidates to supply high quality lubricant base oil for lubricant production. Vegetable oils have several advantages over other raw materials, as they are readily available, relatively low cost, renewable and environmentally friendly.

Melon seed is botanically called *Colocynthis lanatus* or simply *Citrullus lanatus*. It belongs to the genus citrullus of a large plant family called the *Cucurbitaceae* which is made up of 100 genera and 750 species. The *cucurbitaceae* family has remarkable genetic diversity and good adaption that includes temperate locations, arid deserts tropical and subtropical regions. Seed of this family are source of oils (50%) and protein (35%). Egusi is among the 300 species of melon found in tropical Africa and it is cultivated for its seeds, the regions of it cultivation include; Benin, Cameroon, Ghana, Middle East, Nigeria, Togo and some other countries in Africa (Giwa *et al.,* 2013). Egusi is a crawling crop widely grown for its seed which is dishelmed, dried and ground into paste which is added to vegetable soup to give aroma, improve taste and make soup thick (Bello et al., 2012).

Coconut oil or copra oil, is an edible oil extracted from kernel or meat of matured coconuts harvested from coconut palm (*Cocos nucifera*). It has various applications both for domestic, commercial and industrial uses as a result coconut make up to 2.5% of the world vegetable oil production. Because of its high saturated fat content, it oxidize and thus, resistance to rancidification, last up to six months at 24 ^{0}C (75 ^{0}F) without spoiling. Due to its high saturated fat content (similar to that of animal), numerous health authorities' advice against the regular consumption of the oil having potential for high risk of cardiovascular disease.

Coconut oil can be extracted through the following namely:

i. Dry processing extraction that requires the meat been extracted from the shell and dried using fire, sunlight or kilns to create copra. The copra is then pressed or dissolved with solvents to produce the coconut oil.

ii. Wet processing extraction uses raw coconut rather than dried copra, and the protein in the coconut creates an emulsion of oil and water. Despite numerous variations and technologies wet processing is less viable than dry processing due to a 10-15% lower yield, even compared to the losses due to spoilage and pests with dry processing. Wet processes also require investment of equipment and energy incurring high capital and operating costs.

Convectional, coconut oil processors use hexane as a solvent to extract up to 10% more than produced with just rotary mill and expellers. They refine the oil to remove certain free fatty acids to reduce susceptibility for rancidification. Other processes to increase shelf include using copra with moisture content below 6%, keeping the moisture content of the oil below 0.2%, heating the oil to 130-150^{0}C (266-302^{0}F) and adding citric acids.

Methodology

Materials

Two samples which include melon seed (*Citrullus lanatus*) and coconut (*Cocos nucifera*) were brought from Gwari local market in Minna, Niger State. The seeds were kept in an electric oven for 4 to 6hours to reduce the seeds moisture content to ease extraction and improve the quality of the oils. The oils were extracted by the use of oil expeller.

Preparation of oil blends

Both oils were blended at different ratios: 20:80, 40:60, 60:40 and 80:20 (A, B, C and D) respectively at 40 ^{0}C using magnetic stirrer (Siddique *et al.,*2010). The physical and chemical characterization of the oil blends were analysed using a described method or standard.

Acidic Value

A neutral solvent was prepared by mixing methanol and petroleum ether. 1g of the oil was measured and placed in the beaker. 50ml of neutral solvent was added to the oil in the beaker. The mixture was thoroughly stirred for about 30mins. 0.56g of Sodium Hydroxide pellet was measured and used to prepare 0.1MSodium Hydroxide solution (NaOH solution). 4 drops of phenolphthalein indicator was added to the oil/neutral solvent in the beaker and titrated against 0.1M NaOH until end point was reached (ASTM D 664). Melon has an amino acid profile that compares favourably with that of soya beans and even white of egg (Akoh and Nwosu, 1920).

Free fatty acid content

According to Gregory (2005), the acid value obtained was subsequently used to determine the free fatty acid and this was defined by the equation below

$$\text{Acid value} = \text{free fatty acid}/2$$

Specific gravity

Following the ASTM D1298 method, Volume of oil is assumed to be 25ml.Weight of empty bottle is 23.112 and weight of bottle + water is 43.485.The empty calibrated bottle was filled with blended vegetable oil and reweighed; Specific gravity was calculated using the relation:

Density

From theory, the density of a substance is equal to the mass of the substance per unit volume of that substance. Density could also be described as volumetric weight of a substance, in other words, it describes the weight of the substance.

Viscosity from 40 ^{0}C to 120 ^{0}C

The viscosity of the blended oil sample was determined using an empty bottle as a viscometer with a stop watch. The samples of the blended oil were heated to a temperature of 40 ^{0}C, 60 ^{0}C, 80 ^{0}C, 100 ^{0}C and 120 ^{0}C respectively. Initially, the viscometer was calibrated 1cm apart; the oil sample was then poured into the viscometer. At the time which the oil starts dropping into the beaker or conical flask the stop watch is started. The time, at which a specific distance of about 1cm is attained, the stop watch is stop and the time interval is taken or recorded. The procedure was repeated for about two to three times and the average value was taken (ASTM D-445).

Iodine value

Blended oil sample is poured into a small beaker; 1 g of the oil was weighed and poured into a glass-stopper bottle of about 250 ml capacities. 10 ml of carbon tetrachloride was then added to the oil to dissolve. Subsequently, 20 ml of the solution was added and a stopper was inserted and allowed to stay in the dark for 30 minutes. 15 ml of potassium iodide solution (KI), 10 wt% and 100 ml of water was introduced and the mixture was thoroughly mixed and titrated with 0.1 M sodium thiosulphate solution (Na_2SO_3) using starch as indicator.

Pour point

The sample was poured into the test jar to the level mark. The test jar was closed with the cork carrying the high pour thermometer. The position of the cork and the thermometer were adjusted for the cork to fit tightly, the thermometer and the jar were coaxial and the thermometer bulb was immersed 3 mm below the surface of the sample. After this, the test jar was placed into the cooling medium. The sample was cooled at a specified rate and examined at interval of 3 ^{0}C for flow characteristics until a point was reached at which the sample showed no movement when the test jar was held in a horizontal position for 5 seconds. The observed reading of the thermometer was recorded. 3 ^{0}C was added to the recorded temperature and the result was recorded as the pour point (ASTM D – 97).

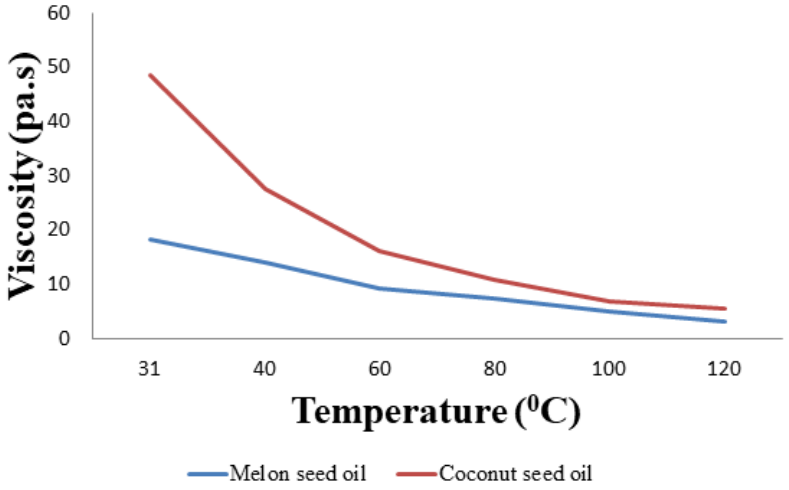

Figure 1: Result of thermal stability of Melon Seed Oil (MSO) and Coconut Oil (CNO)

Cloud point

Approximately, 20g of all the bended oils (samples) were heated to 120 ^{0}C and cooled in cold water bath and stirred. After the sample has reached a temperature 10 ^{0}C above the cloud point, stirring was done steadily and rapidly in circular motion to prevent super-cooling and solidification of the oil crystals on the side or the bottom of the bottle. At this point, the bottle was observed regularly of 2-3mins for the presence of cloudiness when the thermometer was no longer visible or clear.

Flash point

This test was carried out in accordance with the ASTM D – 93. The pensky-Martens closed cup tester was used for this test. The cup was filled with the biodiesel as to the mark set in the interior of the cup. A Bunsen burner was lighted and used to heat the biodiesel; the biodiesel was constantly stirred in order to maintain a uniform temperature. An injector burner was lighted and at intervals of 10 seconds, it was brought to the opening at the top of the cup to see if the biodiesel would ignite or produce a pop sound. The temperature at which this is observed was noted. The procedure was repeated twice and the average temperature was taken and recorded as the flash point.

Saponification

1g of the oil was weighed into a flask. 25cm^3 of 0.1M alcoholic potassium hydroxide solution (KOH) was added into the flask. A reflux condenser was attached and the flask was heated on a water bath for1 hour with constant shaking. At the end of 1 hour the flask was removed from the water bath and 1cm^3 of the 1% phenolphthalein indicator was added. It was then titrated with the standard 0.5M hydrochloric acid.

Hydrogen peroxide

1g of oil was weighed into a clean dry boiling tube, 1g of powder potassium iodide and 10cm of the solvent mixture were added. The mixture was allowed to boiled vigorously for 30sec. the tube was washed twice with 25cm^3 portion of water and the was added to the titration flask. This was then titrated with 0.002M of sodium thiosulphate using starch indicator.

Thermal stability

The thermal stability of the blend oil was measured according to the American Society for Testing Materials (ASTM) method. The range was from ambient temperature of 120^{0}C for the viscosity of the oils and blend oil. The thermal stability was by dipping a 40mL stainless steel viscometer rotor (rotor 1) in a beaker containing the heated blend oil then the rotor was set to a revolution of 60rpm.

Results and Discussion

Acid value

Acid value is an important index of physiochemical property of oil which is used to indicate the quality, age, edibility and suitability of oil for use in industries such as paint and the acid value for the blended vegetable oil with different ratio was determined in other to study the properties of the blended oil. It was determine at different ratio, at 60% MSO and 40% CNO, it was determine to be 1.683mgNaOH/g and it shows that it more suitable than other ratios. This value is considered high when compared with others that the value for oils should be less than 1mgNaOH/g. From the result, 20% of MSO and 80% of CNO and vice versa have the same acid value while 40% of MSO and 60% of CNO and vice versa shows that the acid value decreases from a value of 2.805 to 1.122(Akubugwo *et al*,2008).

Free fatty acid value

The free fatty acid value of the blend oils decreases as the concentration of coconut oil decrease from 80% to 20% due to the high saturated fat content of coconut oil. The FFA value deceases from 1.403mgNaOH/g to 0.561mgNaOH/g. Oil blend ratio 80%:20% has the lowest free fatty acid value due to the low concentration of coconut oil.

Specific gravity

Specific gravity is the ratio of the density of a substance to the density of standard usually water for a liquid or solid and air for gas. The blended vegetable oil has specific gravity of 41g. Specific gravity is related to density and in most cases; the density of a liquid is the specific gravity of the substance time's 1000 kg/m^3 (density of water). Therefore from this, the density of blended vegetable oil at different ratio was determined to be 41g throughout. Density could also be described as volumetric weight of a substance, in other words, it describes the weight of the substance. The lighter the density of the oil, the better it is use for different purposes. The density of the oil varies within the range of 41.365g to 41.475g when blended, which makes it lighter and better.

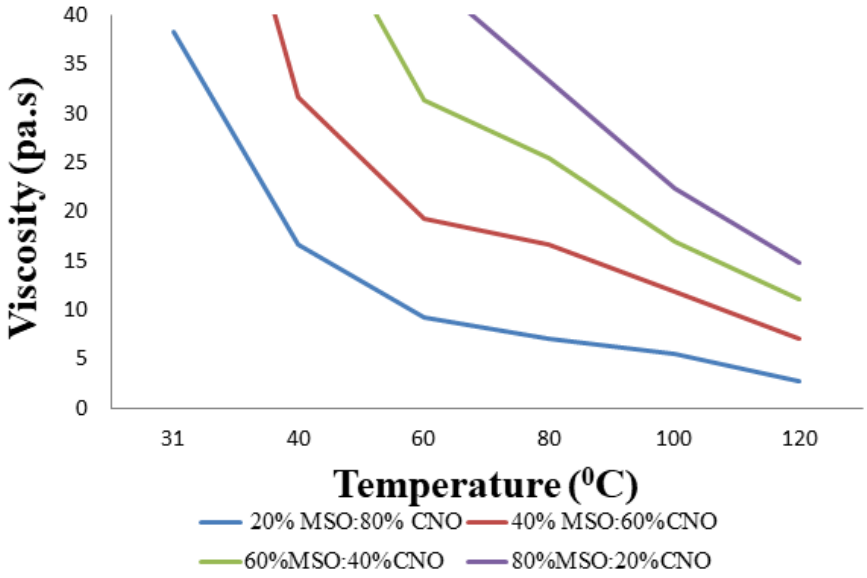

Figure 2: Result of thermal stability of Melon Seed Oil (MSO) and Coconut Oil (CNO) Blends

Density

The result of the density shows a close range of values between 1.653g/mL to 1.659g/mL. This shows that the density of the oil blend increases as the concentration of coconut decreases with an increase in the concentration of melon seed oil. Oil ratio of 80% melon seed oil to 20% of coconut oil has the highest density value and oil ratio of 20% melon seed oil to 80% coconut oil has the lowest density value.

Viscosity at 40 ^{0}C

This is a measure of fluids resistance to flow, the viscosity of the oil at different ratio was determined. At different ratio, the viscosity of the blended vegetable oil was found to be high at 40 ^{0}C this value is slightly lower than that obtained by Giwa *et al*.,(2010) which was found to be 31.52mm^2/s and 32.31mm^2/s obtained by (Bello et al 2010). a higher value of viscosity was found out to cause atomization and operational problem such as carbon deposits, oil ring sticking, thickening and gelling of lubrication oil as a result of contamination by the oil at 120 ^{0}C ,the viscosity of the blended oil was found to be low which makes it preferable for production. From the result of the viscosity of the blended vegetable oil at 40 ^{0} C relatively low for ratio 20% and 80%, and 40% and 60% but increases when the ratio is at 60% and 40%, and 80% and 20%.The properties that were obtained are shown in table 1.

Table 1: Obtained properties of the blended oils

PROPERTIES	**PERCENTAGE OIL BLENDS**					
	20:80	40:60	60:40	80:20	SAE 30	SAE 40
Acid value (mgNaOH/g)	2.805	2.244	1.683	1.122	-	-
Free Fatty Acid (mgNaOH/g)	1.403	1.122	0.842	0.561	-	-
Specific gravity(g)	41.365	41.342	41.467	41.475		
Density (g/mL)	1.653	1.654	1.658	1.659	0.895	0.868
Viscosity @ 40 ^{0}C	16.60	15.10	22.50	22.00	104.00	159.20
Viscosity @ 100 ^{0}C	2.80	4.30	4.00	3.00	12.00	15.87
Iodine value(mgKOH/g)	169	170	181	195	-	-
Pour point (^{0}C)	-1	-1	-1	-3	9	21
Cloud point (^{0}C)	13	13	10	8.00		
Flash point (^{0}C)	302	292	284	276	260	243
Saponification value(mgKOH/g)	112	134	121	163	-	-
Hydrogen peroxide(mgKOH/g)	4.79	4.80	4.91	4.95	-	-

Viscosity at 120 ^{0}C

At 120 ^{0}C the viscosity of blended vegetable oil at different ratios were found to be at lower viscosity which is preferable in production. It was noticed that the values tend to change at different ratios. According to the ratios, it show that the viscosity at 120 ^{0}C tends to increase and also decrease. At the ratio of 20% MSO and 80% CNO the viscosity is low, at ratios 40% MSO and 60% CNO and 60% MSO and 40% CNO the viscosity increases while at the final ratio which is 80% CNO and 20% MSO, the viscosity decreases. This implies that the result does not show if it increases or decreases gradually, it shows that it can increase or decrease at any of the ratios.

Flash Point

The flash point of the blended vegetable oil is the temperature at which the oil will ignite when exposed to a flame or spark. It is a property use to evaluate the flammability of a substance (Gerpen, 2004). Liquid with flash point less than 60.5 ^{0}C or 140.9 ^{0}F depending on the standard being applied are considered flammable while liquid higher temperature of 60.5^{0}C are considered to be combustible. From the result obtain, shows that the flash point value at different ratio was considered combustible and can be used as a biodiesel fuel in some cases (Galadima *et al*.2009). From the result obtain above. The value of the oils at different ratios of the Flash point was found to be in an increasing order from 276 ^{0} C – 302 ^{0} C.

Pour point

Pour point of oil is the lowest temperature at which the oil can flow. The pour point of the blended vegetable oil was determined at different ratios, but the recent ASTM standard do not have limit for pour point too as a result of

the varying climate conditions in different places all over the world (Giwa *et al*, 2013).The result was found out to be in an decreasing order at different ratios of the blended vegetable oil of 20% of MSO and 80% of CNO, 40% of MSO and 60% of CNO and vice versa.

Cloud Point

Cloud Point of oil is the temperature at which the oil begins to cloud and no longer completely soluble in order to determine its physical resistance towards lower temperature. Cloud point is very useful in identifying the minimum temperature of oil storage (Roiaini *et al*., 2014). The results above show that the cloud is the same for percentage ratio 20:80 and 40:60, but decreases gradually when the percentage ratio is 60:40 and 80:20. The cloud decreases from 13^0C- 8^0 C as the ratio of blend of melon to coconut increases.

Iodine value

Iodine value is used primarily in industries; it is of value to us because it gives an indication of the oil stability and health property. Iodine value is a measure of unsaturated fat and oil. It measures the degree of unsaturation of oil at different ratio. The values were determined and found out to be high compared to 114.46/100g and 115.23/100g obtained by (Giwa et al, 2010).At 80% of MSO and 20% of CNO, 40% of MSO and 60% of CNO and 60% of MSO and 40% of CNO have close iodine value while 40% of CSO and 60% of MSO the value increases respectively from 181 – 195g/100g

Saponification Value

The saponification indicates the period the oil could be stored before deteriorating which similar to the peroxide value. The saponification value was found to increase with the storage time of these oils. This explains that with long storage of these oils, fatty acids are likely to be formed which increase the saponification. This also indicates that these long storage degraded oils can play a favourable role in producing soaps and toiletry profitably. The most preferred is at a blending ratio of 40% and 60% with an average saponification value of 134.

Hydrogen peroxide value

The hydrogen peroxide value increased from 4.79 to 4.95 mgKOH/g of blend oil with decrease in the concentration of coconut oil in the blend (reducing from 80% to 20%) probably due to decrease in concentration saturated fatty acids. The high value or low value of peroxide value could also be due to the presence of lower or higher amount of natural anti-oxidation respectively.

Conclusion

The physicochemical properties obtained with the various blends of these oils are within the requirement of some engineering application such as cutting fluids. The oil blend at 60%:40% provides a suitable results for use as a cutting fluid in machining operations with the following properties: acidic value (1.683mgNaOH/g), free acid value (0.842mgNaOH/g), specific gravity (41.467g), density (1.658g/mL), viscosity at 40 ^{0}C (22.50pa.s), viscosity at 120 ^{0}C (4.00pa.s), iodine value (139 mgKOH/g), pour point (-1^0), flash point (284 ^{0}C), saponification value (121 mgKOH/g), Hydrogen peroxide value (4.91 mgKOH/g) and cloud point (10 ^{0}C). These properties are in close agreement with those reported by Lawal *et al.*, (2012). The thermal stability of this ratio is also appreciable for cutting fluid as shown in Figures 1 and 2.

- Based on the above results, the research concludes that blended vegetable oils can be adapted as a suitable substitute for mineral oil in machining operations due to their improved qualities and functionalities.
- Its impact on the environmental and health of personnel during the production chain also confirms with the restrictions on the safety and handling of other lubricant by the environmental agencies (kreivaitis et al, 2010).
- The results also show the necessity for the development of different blends of oil with significantly increased biodegradability as compared to the mineral sources.

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