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Original Research Article

Characterisation and Modification of Mahogany *(Khaya senegalensis)* Seed Oil for Biolubricant Production

***[1]Ayuba, D.M., [2]Abba-Aji, M.A., [3]Hammajam, A.A. and [1]Chinda, A.**

[1]National Centre for Technology Management (NACETEM), Yola, Nigeria.
[2]Department of Mechanical Engineering, University of Maiduguri, Maiduguri, Nigeria.
[3]Nigerian Army University Biu (NAUB), Biu, Nigeria.
*davidayubamshelia@yahoo.com; hammajam@unimaid.edu.ng; birma4real2004@yahoo.com; chindaamos@gmail

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ABSTRACT

Mineral oil-based lubricants are non-renewable, harmful to health and prone to price fluctuations. Thus, vegetable oils are considered as suitable alternatives to mineral oils for lubricant production. Research on the use of non-edible vegetable oils for lubricant development has become necessary. In this study, the oil extracted from mahogany (Khaya senegalensis) seeds was investigated as a feedstock for the production of bio-lubricant. The oil was extracted from the seeds using the traditional method. The oil was characterized, modified for suitability and used to develop lubricants for industrial applications. Commercially available mineral oil based lubricant SAE 20/W50 was used as a control. The acid value, free fatty acid, density and viscosity of the oil were then determined. The acid value, free fatty acid, density and viscosity of the oil obtained were 3.87 mgKOH/g, 2.46%, 0.936 g/cm^3 and 9.5 cSt respectively. The characterisation of the oil produced revealed that the acid value, viscosity, flash point and density were within the standard specified by the ASTM. This is an indication that oil obtained from Khaya senegalensis oil could be used as feedstock for bio-lubricant production.

1. INTRODUCTION

Research has recently targeted alternative biolubricants in resolving the challenges faced by the use of mineral-based lubricants (Ahmad, 2021). Biolubricants can biodegrade easily and fast. (Noreen, *et al.,* 2021). They are also nontoxic to humans, aquatic life and land (Salih, *et al.,* 2011). They may be based on oils extracted from plants, animals or esters manufactured from modified oils. Examples of oil used for biolubricant production include jatropha seed oil, castor seed oil, soybean oil, sunflower oil, amongst others (Odetoye, *et al.,* 2016; Cavalcanti *et al.,* 2018; Kumar, *et al.,* 2021).

Biolubricants are biodegradable and non-toxic to humans and have better physicochemical properties than petroleum-based lubricants and also have higher flash point, higher boiling point, high lubricity, high biodegradability, high viscosity index, low volatility, and less toxic (Cecilia *et al.,* 2020). Biolubricants can be obtained from both edible and non-edible oils. The use of edible oil for the production of bio-oil is not practicable because they are in great urge for fulfilling the requirement of human food. As edible oil is used in the food chain, the use of edible oil as a lubricant can give rise to the ecological damage by using their land (Singh *et al.,* 2019). The employment of non-edible oil as lubricant has various advantages as inedible plants can be cultivated in a harsh environment and do not cause ecological damage, are easily obtainable, low price and biodegradable, and are non-toxic. These biolubricants can be classified according to their chemical composition as natural and synthetic oil. Natural oils are obtained from plant or animal fat by various extraction or distillation process. Synthetic oil uses the natural oil as a basic material and is obtained by chemical modification of natural oils. The natural oil contains triglycerides which are obtained from glycerol and fatty acid chains. The percentage composition of fatty acid in oil affects the physicochemical properties of oils. A fatty acid is a carboxyl acid with a long carbon–carbon chain (Cecilia *et al.,* 2020). Fatty acids are classified based on the presence of double bond in the carbon–carbon chain. Saturated fatty acid is those that do not have double bond, and unsaturated fatty acid has minimum one double bond. Synthetic oil is obtained from chemical modification of natural oil.

Thermo-physical properties of natural oils can be improved by chemical modification. Thermal and oxidation stability can be affected by the presence of the unsaturated part of natural oil. Chemical modification of natural oil is mainly focused on modification of unsaturated fatty acids because double bonds are more vulnerable to oxidation reaction. The most common chemical modification includes the transesterification process, epoxidation process, and hydrogenation process (Cecilia *et al.,* 2020). Epoxidation reaction is the chemical modification of unsaturated part of the natural oil thereby increasing the oxidation stability. Using a variety of reagents including air oxidation, hydrogen peroxide, and peracetic acid, it converts the carbon–carbon double bond into oxiranes (epoxides). Epoxidation reaction results in an increase in thermal and oxidative stability, viscosity and lubricity of natural oil. Another method to advance the thermo-physical properties of lubricating oil is by the application of additives. These additives in lubricating oil are used for different purposes such as to improve the viscosity, viscosity index of the oil, to increase the oxidation stability of oil, and to improve the frictional and wear characteristic of oil. These additives are anti-wear, high-pressure additives, detergents and dispersants additives. The function of this kind of additives is to improve the capacity of lubricating oil to withstand the extreme pressure and thermal condition. Sulfur, phosphorous, and chlorines are this kind of additives, but these are harmful to the environment.

This study aims to extract and characterise the physiochemical, rheological and temperature properties of mahogany seed oil as bio-lubricant and modify it with additives to assess its potential application in lubrication processes.

2. MATERIALS AND METHODS

2.1. Material Collection and Preparation of Samples

Mahogany (*Khaya senegalensis*) fruits were harvested from mahogany plant in shaffa, Hawul Local Government Area of Borno State in April 2023. In Shaffa, the wet season is oppressive and over cast, the dry season is windy and partly cloudy, and it is hot year round. Over the course of the year, the temperature typically varies from 57 ºF to 100 ºF. The rainy period of the year last for 6 to 7 months, from April to October, and the month with the most rain in Shaffa is August, with an average rainfall of 9.4 inches. The fruits were cracked to release the seeds. The seeds were sun dried for three days.

2.2. Extraction of Oil from Mahogany Seeds

A 900 ml pan was set on fire and heat the dehusked seeds for 20 minutes. Thereafter, it was air roasted for 20 minutes. The roasted seeds were removed from the pan and kept under shade for 30 minutes. Finally, the

seeds were crushed with pestle and mortar and further ground into fine powdery form by the use of a traditional grinding stone. Maize stock was collected and burnt to ashes using ceramic crucible incinerator, the ashes were collected, weighed and mix with water in the ratio of 1:4 (v/v). The mixture was filtered, and the solution was collected. Traditional method was used in the extraction of the oil. During this, the finely ground mahogany seeds were mixed with the potash solution, a pot of water was set on fire and allowed to boil, the mixture of the finely ground mahogany seeds and potash were added to the boiling water and stirred continuously until the whole mixture agglomerated, thereafter, a layer of oil appeared on the top surface which was then drained from the pot. The drained oil was allowed to cool at room temperature and was then filtered out.

2.3. Characterisation of Mahogany Seed Oil

Standard procedures according to the American society for testing and materials (ASTM) methods of analysis were adopted in the characterisation of the raw oil and the bio-lubricant produced.

2.3.1. Quantification of the saponification value of vegetable oils

Fresh alcoholic KOH solution was prepared by dissolving the KOH precipitate in ethanol. Over 1 g of oil was carefully measured and transferred into a conical flask. Subsequently, 25 ml of alcoholic KOH solution was added to the flask, and a blank was prepared as well. The flask was tightly covered and placed in an oven for 30 minutes, with periodic stirring. To the mixture, 1 ml of phenolphthalein was added, and the blank and sample were titrated with 0.5 M HCl until the endpoint was reached. The saponification value (SV) was calculated using the Equation (1) according to ASTM D464-15(2020).

$$SV = \frac{56.1\mathrm{X(B-A)XN}}{\mathrm{Woil}} \quad (1)$$

Where; B= volume of standard ethanol potassium hydroxide used in blank titration; A= volume of standard ethanol potassium hydroxide used in titration with the oil; N= normality of standard acid; and Woil = weight of oil used; 56.1= equivalent weight of potassium hydroxide

2.3.2. Acid value and free fatty acid (FFA)

To determine the acidity of the oil sample, 0.002 kg of the oil was placed in a 250 ml glass bottle. A mixture of pet ether and alkanol, which did not react with the oil, was prepared. 50 ml of this mixture was added to the glass container containing the oil sample. The mixture was vigorously stirred by hand for 30 minutes. Separately, 0.56 g of potassium hydroxide (KOH) powder was transferred to a beaker, and a 0.1 M KOH solution was prepared. Three drops of phenolphthalein indicator were added to the oil-ethanol-petroleum ether mixture, and it was titrated with the 0.1 M KOH solution until it reached a soap concentration of 0.1 M. The colour of the mixture changed to pink after adding the 1 M soap, and this colour change lasted for 15 minutes. The acid value (AV) was determined using the Equation (2) according to ASTM D664-18e2 (ASTM 2019)

$$AV = \frac{56.1XVXN}{Woil} \quad (2)$$

Such that; V= volume of standard alkali used; N= normality of specified alkali used;

Woil= used oil weight.

The percentage free fatty acid (%FFA) is obtained from Equation (3)

$$FFA = \frac{AV}{2} \quad (3)$$

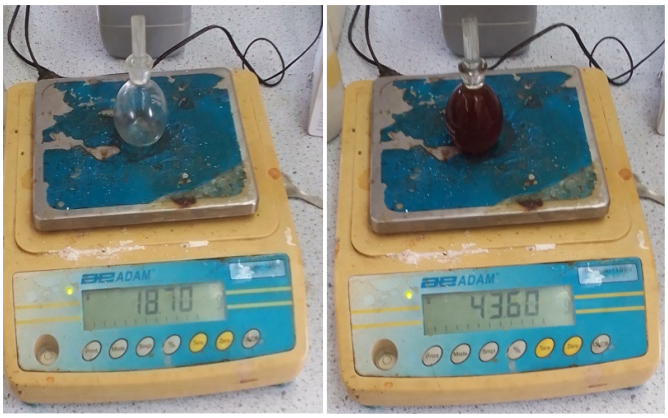
Where FFA = free fatty acid and AV = acid value.

2.3.3. Determination of density

The density measurement was conducted in accordance with ASTM D1298, while the specific gravity was determined following ASTM D1217-12 (ASTM, 2016). To ensure accuracy, a 25ml SEDI-M bottle was thoroughly cleaned using liquid soap, water, and pet ether. Afterward, it was dried in an oven and weighed. The bottle was then filled with distilled water, weighed again, dried once more, and finally filled with the oil sample and weighed, as depicted in Plate I. The specific gravity was calculated by dividing the mass of the weighed oil by the mass of the weighed water, while the oil's density was determined by dividing its mass by its volume, as per theoretical principles. The density of the samples was taken at 30ºC as expressed in Equation (4).

$$D = \frac{M_{BL} - M_B}{V_L} \tag{4}$$

where D is density of liquid (g/cm^3); M_{BL} , the mass of bottle and liquid (g); M_B, the mass of bottle only (g) and V_L is the volume of the liquid (cm^3) (Woma, 2021).



(a) (b)

Plate I: Determination of specific gravity and density; (a) weighing empty density bottle, (b) weighing density bottle with oil sample

2.3.4. Determination of viscosity

The dynamic viscosity of the oil sample was determined following the ASTM D2983-22 (ASTM 2023) standard using a digital viscometer NDJ-5S (model 2013) with a measurement range of 10 to 2 x 10 6 mPas and an accuracy of +2%. The rotor of the viscometer was cleaned and dried using methanol before being attached to the device. The oil sample was poured into a 30 ml sample bottle, and the temperature was measured using a digital thermometer. The sample bottle was then placed on the viscometer stand, and the power switch was turned on. After ten seconds, the viscosity of the oil was displayed on the machine, and the value was recorded. The oil sample was then heated in a water bath to 40ºC and 100ºC, and the viscosities at both temperatures were measured. Hence, the viscosity was converted to kinematic viscosity by dividing with density of fluid (Woma, 2021).

2.3.5. Determination of flash point

The flash point of lubricating oil is the point at which its vapours ignite. Consideration of fire safety, flash points and fire are very important as these are the only factors that determine lubricants' fire hazard. In general, the flash point of oils increases as the molecular weight increases. Flash point was measured according to ASTM D93-20 (ASTM 2020). Oil measuring 30ml was poured into cup and inserted into the

machine (automated Pensky- Martens closed-cup apparatus) and then powered. After the machine finished running the flash point temperature is displayed on the LCD screen as shown in Plate II.

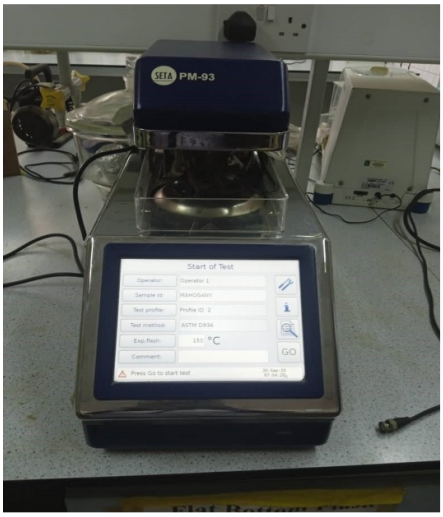


Plate II: An automated Pensky- Martens closed-cup flash point tester (Seta PM-93 35000-0)

2.3.6. Determination of viscosity index

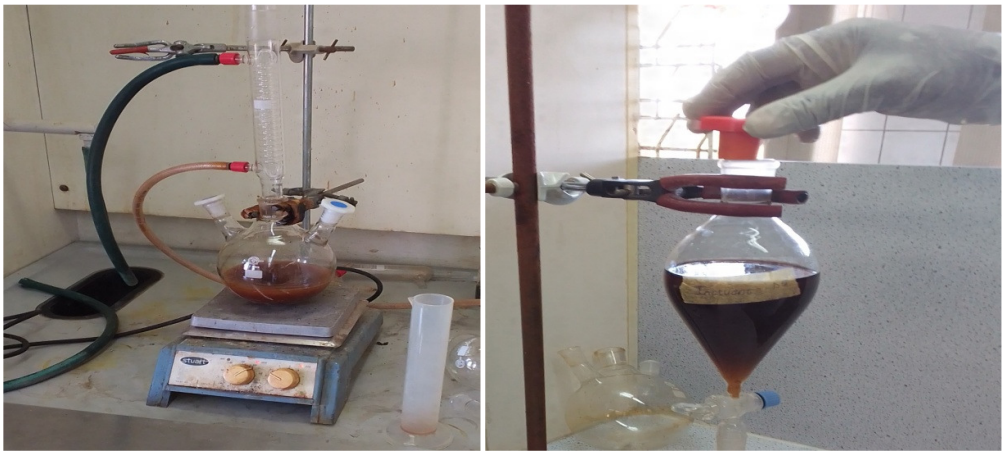
The viscosity index is a measure of how much the viscosity of an oil changes with temperature. Higher values indicate that the oil's viscosity remains relatively stable as the temperature increases. To calculate the viscosity index, the kinematic viscosity of the oil is measured at 40°C (referred to as 'U') and at 100°C. The ASTM D2270-93 (ASTM 1998) standard is used to determine the viscosity at 100°C for the oil being tested, as well as for reference oils labelled as 'L' and 'H'. These values are then used in a formula to calculate the viscosity index. The obtained 'U', 'L' and 'H' were substituted in (6) to yield the viscosity index (V.I) as shown in the Equation (6)

$$V.I = \frac{(L-U)X100}{(L-H)} \tag{6}$$

2.4 Chemical Transformation of Vegetable Oil

Some rapidly biodegradable lubricating oils are obtained from unmodified fresh oils. The triacylglycerol structure of vegetable oil makes it an excellent candidate for potential use as a base for lubricants and functional fluids. However, their thermo-oxidative and hydrolytic stability is unacceptable, and their useless low-temperature behaviour, which occurs under harsh temperature and pressure conditions, shear forces and other tribochemical degradation processes, also hinders their use as base-oils in its natural state (Srivastava and Sahai, 2013). Therefore, native vegetable and animal oils are only used in places with lower thermal stress. An interesting way to solve these problems is the chemical conversion of vegetable seed oils (Asadauskas and Erhan, 1999).Chemical conversion is necessary to improve these technical limitations, eliminate the bisallylic activity of hydrogen in methylene that disrupts many unsaturation, and optimize the range of chemical distortions for better low-temperature applications (Erhan and Asadauskas, 2000; Kalhapure *et al.,* 2015). To avoid the problem of soap formation, a two-step process was used to chemically convert mahogany seed oil into esterified oil. The following subsection describes the details of the chemical modification performed on mahogany seed oil. The oil was modified using acid-catalysed esterification, which is considered a pre-treatment for the actual reaction of crude oil to reduce its water content. Soap formation and thus the reduction of free fatty acids (FFA) is mainly caused by the water content (Ho *et al.,* 2020). The acid-catalysed esterification was carried out according to the method of (Abdullah *et al.,* 2014), with minor changes. The oil was fired up in the glass flask to 60 ºC and a liquid sulphuric acid (1 out of 100 parts based on the oil volume) in methanol (3 out of 10 parts by volume) was fired up to 45 ºC and introduced

into the reaction flask. The resultant fluid was placed in a water bath heated to 60 ℃ and stirred with a mechanical stirrer for 1.5 hours as shown in plate III. The content was then poured into a separating funnel and allowed to settle for 24 hours. The methanol-water fraction at the top layer was removed and the oil was decanted and washed with distilled water until a pH of 7.0 was achieved.



(a) (b)

Plate III: Esterification of mahogany seed oil (a) oil in the reactor being heated (b) mahogany seed oil esterification product in the separation funnel

3. RESULTS AND DISCUSSION

The physico-chemical analyses of Mahogany seed oil revealed the following properties presented in Table 1. The specific gravity of the oil is 0.936, and its density is 936 kg/m^3. This value is slightly lower than value 958.2 kg/m^3 as reported by Abubakar et al.,(2019). However, the value obtained is within the ASTM D4052 standard range of 800-1100 kg/m^3. The variations in these values could be attributed to differences in climate, soil conditions, and testing conditions. The acid number of the mahogany seed oil is 3.87 mg KOH/g, and the percentage of free fatty acids is 2.46. A lower acid number indicates better lubricant performance, as oils with high acid numbers are more likely to cause corrosion and wear on lubricated machine parts. Based on the acid value, it can be inferred that mahogany seed oil may not be an ideal lubricant and would require modification to reduce its acid value and improve its suitability as an industrial lubricant. The saponification value of the mahogany seed oil, which measures its tendency to form soap during organic neutralization, was found to be 160.41 mg KOH/g. The iodine value of mahogany seed oil, which indicates its level of unsaturation and affects oxidation and deposition in internal combustion engines, was measured to be 60.9 gI_2/100 g. This value is lower than the standard value of 115 gI_2/100 g, classifying the oil as non-drying. The pH value of the mahogany seed oil was determined to be 3.87, indicating its acidity. Ideally, a lubricant should have a pH between 8.0 and 10.0 to avoid skin damage and microbial deterioration. The acidic pH of the mahogany seed oil may reduce corrosion protection and shorten the lifespan of lubricated machine components. Therefore, modification of the mahogany seed oil is necessary to make it suitable for use as a lubricant.

Table 1: Properties of mahogany seed oil

Parameter	Mahogany seed oil	SAE 20/W50
Specific Gravity	0.936	0.878
Free Fatty Acid (mg KOH/g)	2.46	----
Saponification Value (mg KOH/g)	160.41	----
Acid value (mg KOH/g)	3.87	----
Iodine Value (gI2/100g oil)	60	80
pH	3.47	7.12

The rheological properties, including viscosity and viscosity index, of mahogany seed oil is presented in Table 2. These properties are crucial in assessing the effectiveness of a lubricant. A higher kinematic viscosity indicates better lubricating capabilities (Rao and Srikant, 2007). The results reveal that mahogany seed oil has a kinematic viscosity of 37.7 cSt at 40 ºC and 9.5 cSt at 100 ºC. This places mahogany seed oil in the ISO VG 32 grade of industrial oil, meeting the required standards.

Table 2: Rheological properties of mahogany seed oil and mineral oil

Parameter	mahogany seed oil	SAE 20/W50
Viscosity at 40ºC (cSt)	37.7	236.9
Viscosity at 100ºC (cSt)	9.5	99.1
Viscosity Index	167.2	65
Dynamic Viscosity at 40ºC (mPas)	35.3	208
Dynamic Viscosity at 100ºC (mPas)	8.9	87

The temperature properties of the mahogany seed oil, including cloud point, pour point, and flash point is presented in Table 3. These properties are essential in determining the oil's performance under different temperature conditions. The cold flow (pour point) of the oil from mahogany seed is (-9 ºC) which is higher than that of the mineral oil lubricant SAE 20/W50. Mahogany seed oil have a relatively good cold flow properties (cloud point and pour point) which have been what is lacking in most vegetable oils that hinder their applications in systems exposed to low temperatures. Thus, mahogany seed oil can be used for lubrication of machines operating in cold climate such as automotive engines, construction machines. The flash point of the mahogany seed oil (200ºC) is lower than that of the SAE20/W50 oil (255ºC).

Table 3: Temperature properties of mahogany seed oil

Parameter	Mahogany seed oil	SAE 20/W50
Pour point (ºC)	-9	-24.1
Cloud point (ºC)	-4	-18.9
Flash point (ºC)	200	255.0

4. CONCLUSION

The characterization and modification of mahogany seed oil revealed that it is denser than SAE 20W/50 but less dense than water, indicating that it would float in water. However, the oil was found to have good lubricant properties but was deficient in wear. These limitations were attributed to the high levels of unsaturation and free fatty acids in the oil. Modification of the mahogany seed oil through acid-catalysed esterification improved its properties, resulting in better cold flow properties.

5. ACKNOWLEDGMENT

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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