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Production of Biolubricant from Parkiabiglobosa Seed Oil through Transesterification

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ABSTRACT: Extracted oil from parkiabiglobosa seed was analyzed for its physicochemical properties such as density, acid value, % free fatty acid (FFA) and saponification value. Findings from the analysis of parkiabiglobosa seed oil reveal that its %FFA of 3.862 was high for transesterification. Its reduction was achieved by esterification with methanol to 0.52. The method employed in the production of lubricant involves double transesterification. While the end product of the first stage yields methyl ester, the second stage produced polyol ester (biolubricant). The produced biolubricant was blended with petroleum base lubricant. Major lubricant properties of the biolubricant and its blend (B10 and B20) including density, specific gravity, viscosity at 40 and 100 ^{o}C, viscosity index and pour point were analyzed and found to be comparable with ISO viscosity grade 46 (ISO VG - 46). Though the pour point of the produced biolubricant is higher than the standard but its blend with petroleum based lubricant give an improved property which conforms to international standard organization viscosity grade - 46 for lubricant.
KEYWORDS: parkiabiglobosa oil, biolubricant, methyl ester, transesterification, lubricant blend.

I. INTRODUCTION

Lubricants are substance incorporated to diminish friction between surfaces in common contact, hence decrease the heat generated when the surfaces move. It might likewise have the capacity of conveying forces, moving unfamiliar particles, or warming or cooling the surfaces [1]. In addition to mechanical applications, lubricants are utilized in bio-clinical applications on patients for artificial joints, ultrasound examination and medical examinations [2]. Lubricants have found many applications for a great many years. In the Roman periods, lubricants were mostly derived from olive oil and rapeseed oil, as well as animal fats.

The growth in lubrication peaked in the Industrial Revolution with the coexisting use of metal-based hardware [3]. Initially depending on natural oils, requirements for such machinery moved toward oil-based materials in the early 1900s. Advancement accompanied the improvement of vacuum refining of oil as depicted by the Vacuum Oil Company. This innovation permitted the filtration of very non-volatile substances, which are normal in many lubricants.

However in recent time conscious and unplanned lubricant destruction to the environment in recent years by means of leakages, spills and even evaporation have prompt significant concerns with respect to contamination and environmental health. Annually, about 5 to 10 million tons of oil based products are released into the environment every year, with 40% occurring from spills, modern and metropolitan waste, urban overflow, treatment facility procedures, and buildup from marine engine exhaust [4]. Consequently, strict specifications on biodegradability, toxicity level, occupational health and safety and discharges have become compulsory in specific applications. Alternate source of lubricant should be technically feasible, environmentally satisfactory, promptly accessible and economically viable for any practical application. From these criteria vegetable oils (triglycerides) prove to be a good renewable alternative lubricant source. Lubricant oils comprise of up to 80% of oil base stocks which give their properties of viscosity, strength and pour point to the lubricant in addition to added substances enhanced to improve these properties [5].

Most lubricant oils exploit in the world contain mineral base stocks comprising of hydrocarbons gotten from heavy fractions obtained from crude oil refining [5]. The composition of these base stocks is intricate, containing particles of various size and structure including branched aliphatic and aromatic hydrocarbons. Vegetable oils have the usage over mineral and artificial base stocks of being an inexhaustible asset that can be produced locally and pose the future option in contrast to fossil carbon-based substrates. Moreover, they can be utilized with no additional transformation, which makes them cost competitive against the greater expenses of artificial base stocks. The fundamental edge of these base stocks is that they are completely biodegradable in contrast with highly contaminant mineral and artificial base stocks [6]. In any case, the utilization of vegetable oils for lubricant formulation has the setback of having lower versatility ranges of use than mineral bases and poor thermo-oxidative stability. Arrangements of estolides by chemically adjusting fatty acids present in the oil can remunerate this absence of versatility [7] or altering double bonds by epoxidation to offer place to a versatile intermediate for the formation of ether branched chains [8]. Revamping the acyl moieties after the hydrolysis of the oil is also another possibility. Another possibility is rearranging the acyl moieties after the hydrolysis of the oil.

Parkiabiglobosa, otherwise called the African locust bean or néré, is a perennial deciduous tree of the Fabaceae family [9]. Found in a wide scope of conditions in Africa, it is fundamentally grown for its pods that contain both a sweet pulp and significant seeds. In regions where the tree is grown, crushing and fermentation of these establishes a significant economic activity. Various components of the locust bean tree are utilized for medicinal uses. However, dating as far back as the 14th century, fermented locust beans have been in use in Africa [9]. The fatty acid composition of parkia seed oil are; palmitic (27.5%), stearic (10.5%), oleic (14.5%), linoleic (44.5%) and linolenic (3.0%) [10].

Researchers have worked on extraction of parkia seed oil [11] and biolubricant production from jatropha [12] and [13] and epoxidation of parkia seed oil [14]. However limited research is available on biolubricant production from parkiabiglobosa seed oil through transesterification method. It is against this background that this research work was carried out to examine the suitability of using Nigerian grown parkiabiglobosa seed oil in biolubricant synthesis using transesterification process with the view of finding a suitable sustainable replacement for the petroleum based lubricant that would help to reduce its adverse impact on the environment.

II. METHODOLOGY

1. Sample Collection and Preparation

Parkiabiglobosa seed was sourced from Kawo market in Kaduna north local Government area of Kaduna state, Nigeria. Dried parkia seeds were reduced in size to smaller particles to build the surface area for oil extraction.

2. Extraction of Oil from Parkiabiglobosa Seed

Oil was gotten from the seeds of parkia by extraction using solvent extraction method with the aid of soxhlet apparatus. A known mass of dried grounded parkia seed sample was measured and placed in a permeable material. The prepared sample was inserted into the thimble and placed in the inner tube of the soxhlet apparatus. The apparatus was fitted with a 500 ml round bottom flask containing n-hexane as solvent. The volume of hexane to weight of seed sample was 6:1. The setup was then positioned on a heating mantle and then heated at a temperature of 60 oC for 4 hr extraction time. The extract was concentrated by means of a rotary evaporator to afford the crude oil and solvent recovered.

3. Esterification of Parkiabiglobosa Seed Oil

This is required to decrease the free fatty acid (FFA) content of the oil as it may lead to high saponification. Esterification reaction using acid (H_2SO_4) as catalyst was carried out as follows to decrease the FFA content of oil which was 3.862%.

Sulphuric acid (H_2SO_4) (1% by oil weight) was added to methanol (30% by oil weight) and mixture was shaken to allow proper mixing. This mixture was added to 291.1g of parkia seed oil which has been heated and stirred at 60^0C on a magnetic stirrer and agitated for 1 hour. In order to ascertain new %FFA, another titration was carried out on the esterified oil which was obtained as 3.79 %. Because the new %FFA of the esterified oil is too high to give the desired result, another esterification was done; using the above formula to bring down the %FFA to 2.10%, third esterification was carried out and the final %FFA result was obtained as 0.52%.

4. Transesterification of Parkiabiglobosa Seed Oil

Transesterification is the reaction of triglycerides to fatty acid alkyl esters (FAAE) and low molecular weight alcohols such as methanol and ethanol in the presence of catalyst. Production (synthesis) of biolubricant involves a double transesterification; the first transesterification is aimed at producing an intermediate product-methyl ester of the oil, and the second uses the methyl ester as reactant to produce the desired product, a polyol ester (lubricant). The two processes were carried out as follows:

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a. Methyl ester Production

This was accomplished by transesterification of the esterified oil with methanol using potassium hydroxide (KOH) as catalyst in the following way; 178 g of the esterified oil was transesterified with methanol. The weight proportion of oil-to-methanol used was 6:1, the amount of catalyst used was 0.5% w/w of the oil and the reaction was conducted at a temperature of 60°C for 2 hour.

After heating and agitating the mixture for 2 hour, the product was transferred into 500ml separating funnel and left for six hour to allow the complete separation of methyl ester from the bye-product (glycerol). Glycerol which is denser than methyl ester settles at the base and separated from the top layer and collected through the funnel into the beaker and hence purified.

b. Biolubricant synthesis

This is accomplished by transesterification of the methyl ester with ethylene glycol in 50 ml batches utilizing 0.5 M Sodium methoxide as catalyst. The weight proportion of oil-to-methanol utilized was 5:1, the measure of catalyst used was 0.6% w/w of the total reactants and the reaction was conducted at a temperature of 120°C for 2 hour.

The parkiabiglobosa oil base biolubricant and petroleum base lubricant were mixed in specified proportions (v/v) to obtain the blends. B10 means 10 percent of bio lubricant and 90 percent of petroleum base lubricant while B20 is 20 percent of bio lubricant and 80 percent of petroleum base lubricant.

III. RESULTS AND DISCUSSION

a. Physiochemical Properties of Extracted Parkia Seed Oil

The result of the physicochemical properties of the parkia seed oil is presented in table 1. The oil yield was determined to be 15.9% which falls within literature value range of 15.9 - 30% for other seed oils [14]. The extracted oil has a pH value of 6.65 which is slightly acidic. The refractive index value obtained falls within the range of 1.447 - 1.590 [15] for other seed oils. The percentage of acid value and FFA obtained are 6.732mgKOH/g and 3.862% for the extracted parkia seed oil. These values are lower in contrast to literature estimations of 9.48mgKOH/g and 4.77% [14] but higher when compared to 1.20 ± 0.065mgKOH/g and 0.81 ± 0.01mgKOH/g for jatropha oil and cotton seed oil respectively [16]. As noted, the higher the acid value of oil, the lower its storage quality and vice-versa [18]. Free fatty acid of oil determines the suitability of the oil for industrial usage. The free fatty acid value of 3.862% is higher than the 1% specified limit for transesterification, hence the oil needs to be esterified. The low FFA likewise proposes low degrees of hydrolytic and lipolytic activities in the oils.

Table 1: Physiochemical properties of extracted parkia seed oil

S/N	Properties	Values
1.	Yield, %	15.9
2.	Refractive index	1.4671
3.	pH	6.65
4.	Pour point, ^{o}C	2
5.	Acid value, mgKOH,/g	6.732
6.	Free Fatty Acid	3.862
7.	Iodine value, g/100g	77.663
8.	Saponification value, mgKOH/g	179.520

Saponification value of the extracted oil was analyzed to be 179.520mgKOH /g. The value is a bit above those reported in literatures for other oils [14], [16]. However, the saponification value obtained conforms with the literature [9],[16]. The saponification value of the parkia seed oil was found to be lower than that of some oils such as palm oil (196 - 205 mgKOH/g), groundnut oil (188 - 196 mgKOH/g), and corn oil (187 - 196 mgKOH/g). The saponification values obtained are comparable with the values for oils such as; shear butter oil (183.1 mgKOH/g), castor seed oil (176 - 187 mgKOH/g), and canola oil (168-181 mgKOH/g). The high saponification value is an indication of the less long chain fatty acids (found in the oil) which have a relatively higher number of carboxylic functional groups per unit mass of the oil contrasted with short chain fatty acids.

Iodine value is the proportion of the extent of unsaturated acids or fat present in vegetable oil. The iodine value was determined to be 77.663 g/100g. The iodine values determined was slightly lower than 82.40 g/100g reported for parkia seed oil [14]. The iodine values obtained were observed to be high when compared to 16.0 g/100g which is the value for Tiger nut oil [9]. Iodine value is a proportion of the level of unsaturation. Thus, oil with iodine value below 90 is classified as non-drying oils, those with iodine value in the range of 110 - 130 are named as semi-drying oil and those with iodine value above 135 are termed as drying oil. The iodine value of the extracted parkia seed oil is in the scope of oils classified as non-drying oils, thus the extracted oil is non-drying oil. The iodine value of 77.663 g/100g for the extracted parkia seed oil is similar to literature values.

b.Characterization of Synthesized Biolubricant and Its Blend

Density is a key property not only in lubricants but in all fluids. It is the proportion of the mass of a substance in association to a known volume. Density plays a critical role in how a lubricant functions as well as how machine perform. Good lubricant oil is expected to have density in the range of 0.8 - 0.9 g/cm3 [17]. From Table 2, the density of the biolubricant, B10 and B20 compared favorably with petroleum base lubricant. Density as property of a fluid is essential for several qualities of a lubricant. This prompts an expansion in the measure of time it takes for particles to settle from suspension. In hydraulic systems, this can be the cause to system failure [17], [18].

Viscosity is an estimation of fluid internal resistance to flow at a specified temperature. For any oil lubrication system, oil viscosity is considered as the most significant parameter. The primary function of lubrication oil is to create and keep up a grease film between two moving metal surfaces and this capacity is very much dependant on the viscosity of the lubricant oil. Approved bodies such as the International Organisation for Standardisation (ISO), American Gear Manufacturer Association (AGMA) and Society of Automotive Engineers (SAE) classified lubricants according to their viscosity at 40°C and 100^{o}C. From Table 2, it can be seen that the viscosity of the parkia seed oil base lubricant, B10, B20 and petroleum based lubricant are in compliance with the standard. It is likewise observed that as the temperature increases from 40°C to 100^{o}C the viscosity decreases.

Table 2: Properties of parkia seed oil base lubricant, its blend, petroleum based lubricant and standard [19].

Properties	Bio lubricant	B10	B20	Petroleum based	ISO VG -46
Density, g/cm^{3}	0.876	0.889	0.873	0.885	- -
Specific gravity	0.885	0.898	0.882	0.825	0.889
Viscosity at 40 ^{o}C,	63.5800	56.760	51.260	10.801	>41.40
Viscosity at 100 ^{o}C,	13.6700	13.340	12.140	3.136	>4.1
Viscosity index	216.690	188.420	194.27	165.4	>90
Pour point, ^{o}C	-2	–5	–7	–9	<-10

However, it tends to be seen that the viscosity of a lubricant decreases as the temperature increases, thus considering Viscosity Index (VI) become important. VI is an arbitrary scalar value that shows the adjustment in oil's viscosity with changes in its temperature. From Table 2, it can be observed that the viscosity index of the parkia seed oil base lubricant, B10 and B20 are in conformity to the standard. Viscosity indexes therefore, an important lubricant property and the higher its value, the more preferable is the lubricant.

Pour point denotes the temperature at which oil ceases to flow when cooled at determined rate in standard apparatus. It is crucial that oil must flow at low temperatures. It is one of the most critical properties which determine the performance of lubricants. From Table 2, the pour point of the blends significantly improved when compared to that of parkia seed oil in Table 1 and biolubricant. The value of -7^{o}C obtained for B20 compare favorably with that of -7^{0}C Jatropha oil base biolubricant [19].

IV. CONCLUSION

The synthesis of biolubricant and its blends from parkia seed oil was successfully carried out through double transesterification by methyl ester production and synthesis of the produced methyl ester. Two blends of B10 and B20 were formulated.

Both blends compared favourably with petroleum based lubricant in terms of density and viscosity at 40oC and 100oC. Though the pour point of the produced biolubricant differ from the standard, but its blend with petroleum based lubricant give an improved property which conforms to international standard organization viscosity grade 46 (VG-46) for lubricant.

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