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Synthesis and Tribological Evaluation of Polyol Based Biolubricant from *Spondias mombin (Anarcadiaceae) Linn*. Seed Oil

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ABSTRACT

Vegetable oil was extracted from *Spondias mombin* seeds and used to synthesize biolubricant via a two-step transesterification reaction. The biolubricant obtained showed an increased viscosity index (293.43), with improved pour point and cloud point properties (2°C and -9°C respectively). he biolubricant showed great potential in lowering the coefficient of friction (COF) (76.6 %) and its mean COF was observed to be within the acceptable range for automotive applications and comparable to commercially available engine oil (SAE20W40).

KEYWORDS: Tribology, *Spondias mombin*, FAME, biolubricant, trimethylolpropane.

1. INTRODUCTION

Lubricants consumed worldwide commonly originate from petroleum, coals, or natural gases[1]. Unfortunately, due to the world's enormous fuel consumption, these sources are limited and will eventually be depleted. This situation has raised interest among the scientific community in finding renewable green materials as replacements for the fossil[2]. With biofuels already gaining traction globally, attention has shifted to biolubricant products.

Biolubricants are chemically modified lubricating oils obtained from vegetable oils that have lubricating qualities comparable to mineral oil-based lubricants. As anti-friction agents, they are crucial for the optimal functioning of equipment by facilitating heat transfer, power transmission, lubrication, and corrosion inhibition[3]. Previous reports have shown that vegetable oil-based biolubricants provide better lubricity than petroleum-based oils[4]. The esterification of free fatty acids in the oil with methanol in the presence of acidic catalysts, and subsequent transesterification to biolubricants using trimethylolpropane (TMP) is the common chemical pretreatment for the conversion of vegetable oils to biolubricants[4,5]. The TMP has been widely reported for use in the formulation of biolubricants from vegetable oils due to the presence of branching which makes the biolubricants exhibit good thermal-oxidative stability and good low-temperature properties[6-8]. In this study, *Spondias mombin* seed oil was used to synthesize biolubricant via transesterification reaction with TMP and assessed for its tribological property.

2. MATERIALS AND METHODS

2.1. Materials and Solvents used

All reagents used were of analytical grade purchased from Sigma and Aldrich. *Spondias mombin* fruit seeds were obtained from Oro village in Isin L.G.A. of Kwara State, Nigeria. The sample was identified at the Herbarium, Department of Botany, Ahmadu Bello University Zaria, Nigeria. The flesh was removed from the seeds by washing with water and the kernels were sundried for 7 days, ground with a milling machine, sieved, and then stored in an oven at 40 °C to constant mass.

2.2. Extraction of seed oil

The pulverized seed sample (3 kg) was extracted by Soxhlet apparatus using n-hexane as the refluxing solvent at 69 °C based on the (NF V03-924) protocol. The crude oil was recovered under vacuum pressure using a rotary evaporator (Model No. HV-2199A, Hoverlabs/India). The extraction yields were evaluated gravimetrically thus;

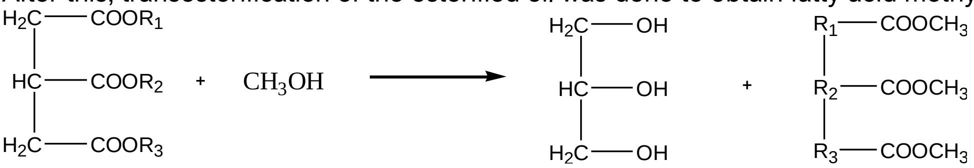
$$W = \frac{m_2 - m_1}{m_0} \times 100 \quad (1)$$

where, W: extraction yields, m_2: mass of the balloon containing the extracted, m_1: mass of empty balloon, and m_0: mass of the vegetable oil sample.

The extracted oil coded SMSO was characterized for its physicochemical properties using standard methods[9]. The oil was also subjected to analyses using Gas chromatography-mass spectrometry (GC-MS) and Fourier transform- infrared spectroscopy (FT-IR).

2.3. Oil Esterification

The synthesis of fatty methyl esters (FAME) was carried out as reported by Ebtisam *et al*. [10]. The oil was initially esterified with methanol and H_2SO4 to reduce the free fatty acid and prevent saponification. After this, transesterification of the esterified oil was done to obtain fatty acid methyl esters (FAME).



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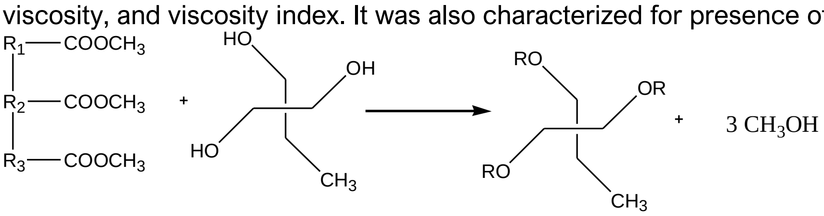
The synthesized FAME was characterised for pour point, cloud point, viscosity, and viscosity index, in addition to functional group analysis using Fourier transform infrared spectroscopy (FT-IR).

2.4. Synthesis of Biolubricant

Biolubricant was synthesized by transesterification of the methyl ester with TMP according to Ghazi *et al*.[11]. The synthesized biolubricant was characterized for physicochemical properties pour, cloud and viscosity, and viscosity index. It was also characterized for presence of functional group using FT-IR.



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2.5. Tribological Evaluation (Frictional Test)

The study of the coefficient of friction was carried out using a pin-on-disc tribometer in accordance with ASTM G-99 standards as reported by Thottackkad *et al*.[12]. A load of 10 N was applied at 10 cm/s and 5 min test duration and the temperature was maintained at 27 °C throughout the whole test process. The process was performed on the biolubricant, SAE 20W40 commercial lubricant and without lubrication.

3. RESULTS AND DISCUSSION

3.1. Physicochemical properties of vegetable oil

The results of the physicochemical properties of the seed oil are shown in Table 1.

The extracted *Spondias mombin* seed oil (SMSO) was observed to be strong and dark golden brown in colour with an oil yield of 10.9 % as shown is Table 1.

Table 1: Physicochemical properties of the extracted *Spondias mombin* seed oil (SMSO)

Seed Oil Property	Seed oil	FAME	Biolubricant
Colour	Dark golden brown	-	-
Oil Yield (%)	10.9	70.25	92.16
Density (g/cm^3)	0.826	-	-
Acid Value (mgKOH/g)	35.3	1.06	-
Free Fatty Acid (%)	17.6	0.53	-
Viscosity @ 40° C (*cSt*)	6.67	14.28	119.05
Viscosity @ 100° C (*cSt*)	1.90	3.81	30.48
Viscosity Index	47.95	167.48	293.43
Cloud Point (° C)	-	13	2
Pour Point (° C)	-	4	-9

Eromosele and Paschal[13] observed an oil yield as high as 31.5% using petroleum ether as the solvent of extraction. Moreover, Orhevba and Osho[14] obtained a closely related yield of *Spondias mombin* seed oil (10.8 - 13.4 %). This may be influenced by the moisture content of the seeds and temperature during extraction[14].
The percentage yield of SMSO biolubricant obtained was 92.2% as shown in Table 1 which shows that the transesterification process was close to completion. This was also similar to the yield (92 %) obtained by Sen *et al*.[7] and (94.12%) by Ifeanyi-Nze and Akhiehiero[15]. The specific gravity and density of the oil were 0.827 and 0.826 respectively. This value was closely related to results (0.825 gcm^{-3}) obtained by Orhevba and Osho[14] and (0.867 gcm^{-3}) by Eromosele and Paschal[13]. The kinematic viscosities of SMSO at 40 ^{o}C and 100 ^{o}C are presented in Table 1 and were determined to be 6.67 *cSt* and 1.90 *cSt* respectively. The viscosity index was also determined to be 47.95. Jumat[16] reported a viscosity of 74 for cotton seed oil and Shah *et al*. [17] reported a viscosity of 32 for *Jatropha curcas* seed oil also both at room temperature.

Improved kinematic viscosities were observed after transesterification of vegetable oil (6.67*cSt*, 1.90 *cSt*) to FAME (14.28 *cSt*, 3.81 *cSt*) at 40 ^{o}C and 100 ^{o}C respectively. Furthermore, an impressive increase in kinematic viscosity was observed at formulation with TMP with the biolubricant, exhibiting viscosities of up to 119.05 at 40 ^{o}C and 30.48 at 100 ^{o}C. This implies that the addition of TMP to the synthesized FAME improved the viscosity of the formulated biolubricant. The biolubricant can thus be classified as an ISO VG 100 lubricating oil according to the ISO standard 3448/ASTM D 2422 (ASTM, 2021). This also implies it is in the same class as SAE 30 oil, which is used for marine applications in a ship's engine room[18]. The VI of the SMSO biolubricant was determined to be 293.43.
The pour point and cloud point of the SMSO biolubricant were determined to be -9 ^{o}C and 2 ^{o}C respectively as shown in Table 1. It has been reported that the presence of ternary alcohols, such as TMP, diminishes the pour point and cloud point of biolubricant[19]. It is assumed that the presence of a large branching group at the mid-point of a fatty acid chain creates a steric barrier around the individual molecule and inhibits crystallization, the result of which is lower pour and cloud points [20].

3.2. GC-MS Profile of Vegetable oil

The GC-MS analysis was carried out on the vegetable oil to determine the fatty acid composition of the vegetable seed oil as shown in Table 2. The oil contained predominantly long-chain monosaturated fatty acids. Abiodun *et al*.[21] also reported the presence of Lauric acid, phenolic lipids and fatty alkanes in *Spondias mombin*.

Table 2: GCMS profile of extracted vegetable oil

RT	Fatty Acid	Area%	Profile
19.027	Lauric Acid	0.75	medium-chain saturated fatty acid
19.337	Oxirane, tetradecyl-	1.79	Fatty Acyls
20.882	Oleic Acid	59.4	long-chain monounsaturated fatty acid
21.067	9-Octadecenal	10.33	Lipids - Fatty Acyls
21.296	Carbamic acid ester	12.2	Carboxylic ester
22.888	Cresol	10.82	Phenolic lipids
31.461	2-(aminomethyl)-cis-cyclopentanol	0.74	Lipids - Fatty Acyls
31.548	11-Tetradecyn-1-ol acetate	0.88	Carboxylic ester
31.64	9-Octadecenoic acid (Z)-2-hydroxy-1-(hydroxymethyl) ethyl ester	0.32	Methyl esters
31.72	Cyclooctaneacetic acid, 2-oxo-	1.25	Carboxylic acids
31.8	Behenic acid	1.51	Long-chain saturated fatty Acid
		99.99	

3.3. FT-IR profile of Vegetable oil, Biodiesel and Biolubricant

As presented in Figure 1, absorption bands in the region of 2855–3000 cm^{-1} and 1375.4–1461 cm^{-1} are due to C–H stretching vibration, which indicates the functional group of alkanes in its molecular structural.

The vegetable oil was observed to have adsorption bands at 1744 cm^{-1} and 1710 cm^{-1} which indicate C-O stretching vibrations characteristic of carboxylic acids, which were observed to slightly shift to 1750 cm^{-1} after transesterification. This result gives evidence to the formation of the methyl ester as suggested by Ebtisam *et al*.[10]. The peaks at 1450 cm^{-1} and 1236 cm^{-1} are characteristic of the C=C and C-H stretching respectively

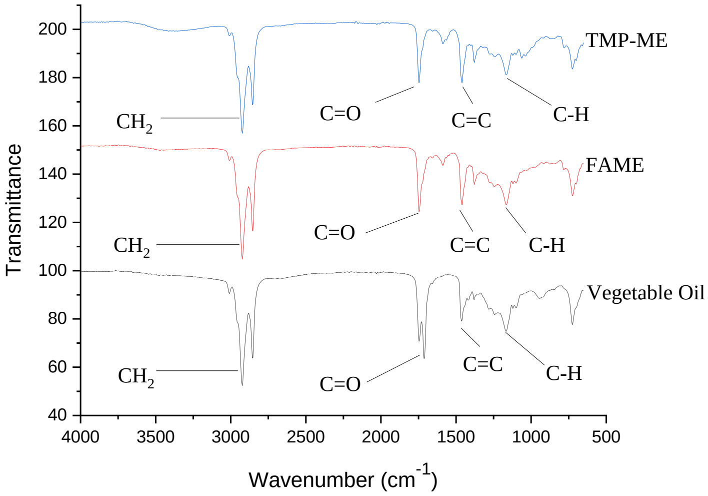

Figure 1. FTIR profile of vegetable oil (VO), Biodiesel (BD) and Biolubricant (TMP)

3.4. Tribological Evaluation

Generally, the biolubricant was observed to exhibit a coefficient of friction of 0.103 as shown in Figure 3. This value compares favorably with the value of conventional lubricant SAE20W/40 (0.106). The coefficient of friction of the biolubricant was to be within the acceptable range of coefficient of friction of a lubricant to be used for a wide range of automotive applications (0.01 – 0.14) reported by Habibullahi *et al*.[22]. As is common with biolubricants, the fatty acid constituent has an affinity for metallic surfaces in a tribo-pair which tends to make it reliable in reducing friction and wear. Also, the utilization of trimethylolpropane in the transesterification process results in removing the hydrogen molecules associated with beta carbon position which further results in improving the thermal stability of the TMP triester.

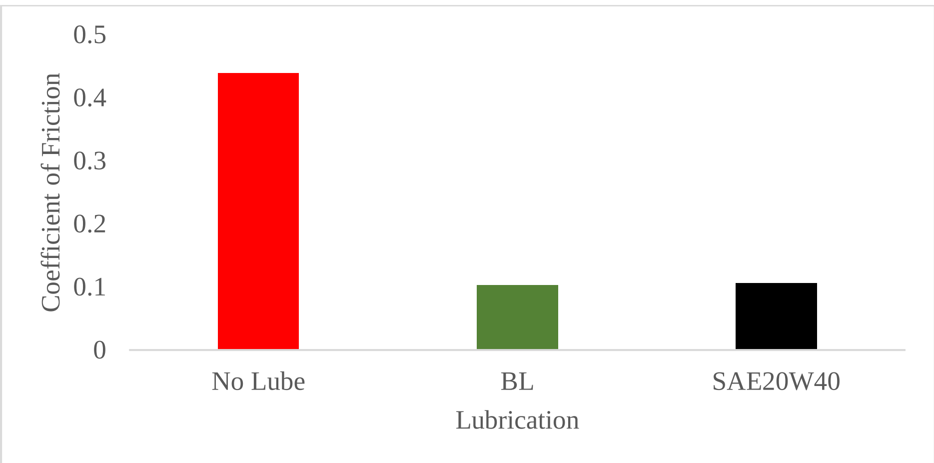

Figure 2. Mean coefficient of friction of biolubricant, standard lubricant and without lubrication

4. CONCLUSION

Vegetable oil derived from *Spondias mombin* seeds by soxhlet extraction was found to be rich in long-chain monounsaturated fatty acids, which makes it suitable for biolubricant production via transesterification with trimethylolpropane. The tribological evaluation of *Spondias mombin* based biolubricant demonstrated effective tribological solutions in moving parts of equipment, comparable to standard and commercially available lubricating oils.

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