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Synthesis of Eco-Friendly Biolubricant by Chemical Modification of Sandbox Seed Oil

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Abstract- To reduce fossil fuel dependence and greenhouse gases, biomass energy is in high demand. Sandbox tree is a widely distributed plant in Abia state and yet, its seed oil is unsuitable for consumption. In this study to determine the usability of sandbox seed oil as a feedstock for biodiesel and biolubricant production, the sandbox seeds were collected from Uturu local government of Abia state. This work centered on modification of sandbox oil (SBO)extracted from sandbox seed (SBS), for possible use as biolubricant. Solvent extraction method was used for extracting oil from the seed. The oil modifications were done using transesterification method with trimethylolpropane. The physicochemical characterizations of the SBO and SBO biolubricants samples were done using standard methods. Furthermore, the oil samples were characterized by Gas chromatography (GC) and Fourier Transform Infrared (FTIR) in other to determine the fatty acid compositions and functional groups respectively. Results showed that transesterification method with trimethylolpropane produced a good lubricant. Temperature, time and particle sizes were the factors affecting the extraction of sandbox oil. The viscosities at 40 °C and 100 °C, viscosity index, specific gravity, pour point, and flash point values of sandboxoil biolubricant (SBOBLT) samples were 48.43 cSt, 11.65 cSt, 139, 0.990 g/ml, -11 °C and 235 °C, respectively. It is concluded that while SBO gave relatively high yield of oil, sandbox oil biolubricant sample exhibited high biolubricant properties.

Indexed Terms- Synthesis, Eco-Friendly Biolubricant, Chemical Modification, Sandbox Oil

I. INTRODUCTION

The increase in carbon monoxide (CO) and hydrocarbon (HC) concentration in the atmosphere due to fossil fuel consumption has posed a lot of danger to the environment and human health. According to a report, the use of petroleum oil in lubricant engines results in an annual emission of around 15 billion tonnes of CO [1]. There is also a great concern that the fossil fuel energy which is not renewable could be exhausted soon. Biolubricant is a promising alternative fuel source because it is environmentally friendly and renewable. Biolubricant has benefits over fossil fuel such as biodegradability, high combustion efficiency, low sulphur, and low gas emission [2]. Biolubricant produces fewer particulate materials, low idle noise and easy cold starting when in use [3]. It also has high lubricity than any other fuels, less toxic, having a higher flashpoint, pour point, cloud point and high cetane number than lubricant. Its demand has had a positive influence on world economy [4] Biolubricants are produced from edible and non-edible oils. The use of edible oils is no longer promoted because it is already over utilized for food supply and will lead to competition. Also, if edible seed oils are utilized as a feedstock for biolubricant, its high cost will influence the production cost of the biolubricant i.e., its production cost increases. Due to this impediment the non-edible oils are majorly used to produce biolubricant. The advantages of producing biolubricant from non-edible seed oils includes its availability in abundance, low production cost, high oil yield, and above all, it does not conflict or compete with food products.

Generally, four methods are used to produce biolubricant from oil extracted from seeds and animal fat. The methods are direct use and blending, transesterification and trimethylolpropane process, pyrolysis, micro emulsion. By direct use and blending, the animal fat or vegetable oil can be used as a fuel in direct injection engines; it has a good heating value and could give a sufficient power [5]. Pyrolysis is a thermal cracking process used to convert the complex structure of hydrocarbons into its simplest structure with or without catalyst. These processes help to reduce the density and viscosity of the oil, thereby affecting the atomization of the engines positively. Fuel produced by this process can be used directly in lubricant engines without any modification [6]. The micro emulsion is defined as thermodynamically stable, isotropic liquid mixtures of oil, water and compounds that lower the surface tension of a liquid and the interfacial tension between the two liquids. This process will solve the problem in viscosity and some other atomization properties of oil [7]. The transesterification and trimethylolpropane process is a reaction between triglycerides in the oil and alcohol which produces the biolubricant (mono alkali ester) and glycerol. This is the most adopted method in biolubricant production. The yield of biolubricant through transesterification and trimethylolpropane process depends on the nature of catalyst.

Catalysts used in biolubricant production are either homogeneous or heterogeneous. Homogenous catalyst in alcoholysis process could be acid or base depending on the amount of free fatty acid present in the feedstock [8]. Base catalyst transesterification and trimethylolpropane process is used when the amount of free fatty acid (FFA) in the oil is low. Potassium Hydroxide (KOH), sodium methoxide and sodium hydroxide (NaOH), are mostly used as base catalysts [9]. When the oil has more than 1% FFA, acid catalyst transesterification and trimethylolpropane process is first carried out before the base catalyst transesterification and trimethylolpropane process [10]. Alternatively, heterogeneous catalyst could be used to tranesterify oil with FFA greater than one. Alkaline metal carbonates (Na2CO3, K2CO3), alkaline earth metal carbonates (CaCO3), alkaline earth metal oxides (CaO, MgO, SrO, BaO), and other oxides such as ZnO are the heterogeneous basic catalysts that have received the most research. [11, 12, 13, 14, 15]. Catalyst is one of the factors that affect the yield of biodiesel.

The yield of the biolubricant depends on temperature, reaction time, agitation speed, choice and ratio of catalyst and alcohol/Oil ratio. The interaction between these factors affects the yield of biolubricant productions and their control is essential to optimize performance [16].

With increasing environmental pollution occasioned by overdependence on synthetic petroleum products and the concerns raised in the recent report from the intergovernmental panel on climate change (IPPC, 2018) emphasizing on the urgency of action to halt greenhouse gas emission by 2030 to achieve the Paris Agreement (COP21) aspirational target of stabilizing global temperature at above pre-industrial levels, there is a need to make a paradigm shift from using products that emits carbon into the environment. Petroleum based lubricant are non-biodegradable and emits carbon compounds when exposed to heat. To overcome this challenge, modification of crude vegetable oil to produce better quality bio-lubricant that are biodegradable and has better oxidative stability has been in compelling need.

Biolubricant is a promising alternative fuel source with benefit over petroleum-based fuels. With the daily increasing need for diversification in energy sources, biolubricant production is being taken more seriously and various approaches are adopted. This has propelled this research to produce environmentally friendly fuel (biolubricant) from sand box seed oil aimed at solving problems faced using fossil fuels when operated on biolubricant engine. Consequently, producing biolubricant from sand box seed oil promotes the use of waste matter industrially, and economic growth of a nation. Disparity in the percentage yield of biolubricant with NaOH and KOH which are the major homogeneous catalysts used in the literature reviewed has necessitated this research, to know from the two catalyst which will produce the higher yield when used in the methanolysis of sand box seed oil. As part of waste management, the knowledge to use sand box seed oil for biolubricant production was born especially in Nigeria where waste management is a challenge. Also, the advantages of biolubricant over diesel as a renewable, sustainable fuel of low inflammable property and gas emission are what motivated this research on biolubricant production.

According to Thangaraj and Raj (2014), transesterification is a chemical process in which one ester is changed into another by exchanging the alkyl group. Alcoholysis (the reaction of an alcohol on an ester), acidolysis (the reaction of an acid on an ester), or esterolysis (the reaction of an ester on another ester) can all be used to carry out this reaction. The oil may undergo any of these three transesterification processes [16]. Unmodified vegetable oil has poor hydrolytic stability, poor oxidative stability, and poor low temperature performance because to its structural flaws. Changing the structure of the oil by converting it to a new form of ester termed polyol ester (PE) is one method that might improve the qualities of the vegetable oil. By removing the hydrogen atom from the vegetable oil's b-carbon structure, this technique gives esters a high degree of heat stability that is uncommon in vegetable oil [17]. Both chemical and enzymatic catalysts can be used to catalyse the transesterification (TER) process for the manufacture of biolubricants. The following stoichiometric equation illustrates the transesterification of trimethylolpropane (TMP) to produce biolubricant from sandbox oil methyl esters (SBOL).

II. MATERIALS AND METHODOLOGY

2.1 Materials

2.1.1 Procurement of materials

Sand box seeds were obtained from Achara Uturu, Abia State, Nigeria. The apparatus and reagents available in Chemical Engineering Laboratory, Gregory University Uturu were used in carrying out the experiments. Trimethylolpropane was purchased from Sigma Aldrich, Germany. Methanol (99 %), sulphuric acid (H_2SO_4), Orto-phosphoric (H_3PO_4) and analytical grade n-hexane were purchased from Conraws Chemical Limited Aba, Abia State Nigeria.

2.1.2. Items of Equipment and Reagents Used.

The equipment, apparatus and reagents used include Reflux apparatus, 500ml three-neck round bottom flask, Kipps apparatus Hot plate with magnetic stirrer, Retort stand, Pipette, 500ml separating funnel, Thermometer, 250ml and 500ml beakers, Water hose, Kinematic viscometer, Digital weighing balance, Gas chromatography (GC) (102AF Gallenkomp England), Fourier Transform Infrared Spectroscopy (WQF-530 FTIR), Oven, Flash point tester, Pour point tester, N-hexane, Methanol, Sulphuric acid, Anhydrous sodium carbonate (Na_2CO_3), Calcium hydroxide, Orthophosphoric acid (H_3PO_4), Potassium hydroxide (KOH), Isopropyl alcohol, Phenolphthalein, Sodium hydroxide, Glacia acetic acid, Chloroform, Potassium iodine, Heating Mantle

2.1.3. Analyses and Laboratory locations/Laboratory Equipment and Models

Table 3.1 and 3.2 show the major analyses and laboratory locations and equipment used.

Table 3.1: Major Analyses and Laboratory Locations

Analyses	Laboratory Location
Oil Extraction	Chemical Engineering Lab GUU
Chromatography/Mass Spectrometry (GC-MS)	Pharmacy Laboratory GUU
Fourier Transform Infrared Spectroscopy (FTIR)	Pharmacy Laboratory GUU
Viscosity	Chemical Engineering Lab GUU
Flash Point	Biochemistry Laboratory, GUU
Pour Point	Biochemistry Laboratory, GUU
Free fatty acid	Biochemistry Laboratory, GUU

Table 2.2: Laboratory Equipment and Models

Laboratory Equipment	Model
Kinematic viscocity @ 40 °C	Sevatis Kinematic Viscometer RC-35
Kinematic viscocity @ 100 °C	Sevatis Kinematic Viscometer RC-35
Pour point tester	Tamson TVB445
Chromatography/Mass spectrometry (GC-MS)	Lawler manufacturing Corp. GC 102AF
Fourier Transform Infrared Spectroscopy (FTIR)	Buck Scientific Spectrophotometer Model 530
Thermostated hot plate	Thermo Scientific I mono Direct
digital weighing balance	JE2002

magnetic stirrer	Model MS7-H550-S^{LED}
Stopwatch	KADIO® KD-6128
Drying Oven	DHG-9023A
Thermometer	Hanna HI-9063

2.2 Methodology

American Society for Testing and Materials (ASTM) standards and methods were adopted for the entire production process.

2.2.1 Sample preparation and oil extraction

The seeds were removed from the epicarp, cracked and air dried for two weeks. Then the seeds were grinded into powdered form stored in an airtight container prior to oil extraction.

Solvent extraction method was adopted in the extraction of oil from the pulverized pulp using soxhlet apparatus. The soxhlet extractor's spherical bottom flask was filled with standard hexane while the ground pulp was placed within the extractor's extraction chamber. The whole set-up was then mounted on a heating mantle and allowed to reflux for some hours. The condensed extract (oil and n-hexane) were heated at a temperature of 60^{o}C using a rotary evaporator to isolate the free flow lipid from the solvent. The extracted oil was subjected to heat in an oven at 100^{o}C to eliminate any moisture and solvent that may be present. The weight of the oil produced was then measured and thereafter the percentage weight of oil produced from the seed was calculated using Equation 1.

$$BY = \frac{W1}{W} \times 100 \qquad (1)$$

Where, W = weight of African star apple seed used (g); W_1 = weight of oil obtained (g).

2.2.2. Solvent Extraction of Sandbox seed oil

Oil extraction from the milled sandbox seed sample was carried out according to Association of Official Analytical Chemists (AOAC) 963.15 method (AOAC, 1990) using soxhlet extractor unit for the five (0.5, 1.0, 1.5, 2.0, and 2.5 mm) Varying average particle sizes. Soxhlet extractor was chosen in order to enhance the solubility of sample in the chosen solvents used. 120g of milled sandbox of a particular average particle size were packed in a thimble of the soxhlet extractor and the extractor was filled with 150 ml of n-hexane. Oil extraction was performed at temperatures of 35, 40, 45, 50, and 55 °C using n-hexane. For each temperature, extraction was performed for five average particle size (0.5, 1.0, 1.5, 2.0 and 2.5 mm). At a specific temperature and particle size, extraction was carried out for 30, 60, 90, 120, and 150 min. The oil yield obtained at the end of every extraction time for every extraction condition was calculated and recorded. The extraction temperature was measured using an electronic thermometer [18], while the time was measured using a stopwatch. AOAC method no. was used to compute the oil yield (see equation 3.1). 920.85 at the end of each extraction. After each extraction batch/cycle, the solvent was removed at 60 °C using rotary evaporator (model N- 1000S-W, EYELA, Tokyo, Japan). The solute to solvent ratio used for the entire extraction was 1:5 (15 g: 150 ml). The entire extraction process carried out under each set of conditions was performed three times and the average values reported, while the total extraction yield was obtained using AOAC 920.85 standard method.

The oil yield of sample was calculated using equation 2.

$$\%\ \text{Oil yield} = \frac{\text{weight of oil extracted (g)}}{\text{weight of sample (g)}} \times 100$$

(2)

The extracted oil sample was sandbox oil (SBO).

Plate 2.1 Sample preparation and Solvent Extraction of Sandbox seed oil

2.2.3 Characterization of the extracted oil

The physiochemical properties of the sand box seed oil produced were determined following American Society for Testing and Materials (ASTM) methods.

2.2.3.1 Colour and flavour

The colour of the oil sample was determined by observation using several independent competent individuals. Oil colour was correlated using color charts. The taste and odour were likewise determined.

2.2.3.2 Specific Gravity (SG)

The specific gravity of the oils was determined by measurements using a specific gravity bottle.

2.2.3.3 Moisture content

The moisture content was obtained by using a known weight of the oil sample put into a clean previously weighted beaker and dried in an oven at 105°C for 4 hours. The sample was taken from the oven, cooled in a dessicator for about 30 minutes and then weighed. The procedure was repeated until a constant weight is obtained. The percentage moisture in the seed was then calculated.

2.2.3.4 Acid Value

The acid value of the sample oil was determined by dissolving about 5.0-5.5g of the sample oil in a hot mixture of 25ml diethyl ether and 25ml 95% v/v ethyl alcohol. The hot solution was neutralized with 0.1 M NaOH using phenolphthalein as indicator. The acid value and free fatty acid was calculated.

2.2.4.5 Iodine Value

0.5g of the oil was weighed into an iodine flask and dissolve 10mL of chloroform. 25mL of Hanus iodine solution was added using a pippete, draining it in a definite time, mixed well and allowed to stand in dark for exactly 30mins with occasional shaking. 10mL of 15% KI was added and thoroughly mixed with 100mL of freshly boiled and cooled water, washing down any free iodine on the stopper. This mixture was then titrated against 0.1N sodium thiosulphate until yellow solution turns almost colourless. A few drops of starch were added as indicator and titrated until the blue colour completely disappears. A blank titration was also run without the sample.

2.2.3.6 Saponification Value

2g of the oil sample was weighed into a 250ml conical flask. 25.0ml of 0.5N alcoholic potassium hydroxide was added. The flask was heated on a steambath, under a suitable condenser to maintain reflux for 30 mins, frequently rotating the contents. 1ml of phenolphthalein was added and the excess KOH was titrated with 0.5N hydrochloric acid. A blank determination without the sample was then performed.

Saponification value was calculated using:

$$Result = [Mx\ (Vb - Vt)\ XN]\ /\ W$$

Where;

M = molecular weight of potassium hydroxide, 6.11

Vb= volume of 0.5 N hydrochloric acid consumed in the blank test (ml)

Vt= volume of 0.5 N hydrochloric acid consumed in the actual test (ml)

N= exact normality of the hydrochloric acid

W= weight of the substance taken for the test (g)

2.2.3.7 Ash Content

Ash content was determined by weighing about 5g of the oil sample using platinum foil. The oil was evaporated to dryness in a steam bath and then the foil and its content was transferred into an oven and ignited to 600˚C. The foil was then weighed with the resulting residue until a constant weight was obtained.

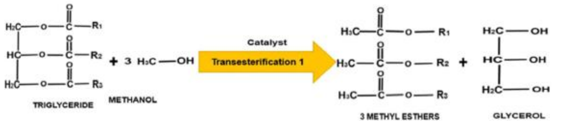
2.3 Transesterification procedure

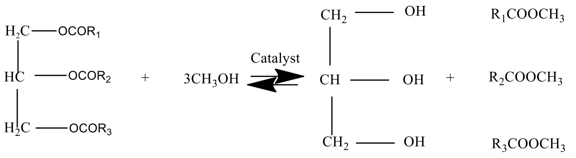
Acidity greater than 1% has been evaluated in advance for crude sand box seed oil. This required neutralization of the oil with a methanolic solution of potassium hydroxide before preheating. Under stirring, a methanolic solution of 1.1% potassium hydroxide in a methanol/oil ratio of 6 was added. After an hour of agitation of the mixture at 60˚C, a settling time of 10 hours or more was followed to enabling the reaction to be driven to completion by allowing the mixture to separate into two layers of biodiesel and glycerol. The glycerol at the bottom was drained off by gravity and the surplus methanol in the biodiesel was removed in an evaporator. The biodiesel was washed in distilled water to enable the further removal of impurities. The washed biodiesel was dried. This process was repeated using NaOH as catalyst.

The percentage methyl ester yield of the sandbox oil sample was calculated using the relationship in equation 3.2:

$$\%\ \text{Methyl ester yield} = \frac{\text{Mass of methyl ester produced (g)}}{\text{Mass of oil sample used (g)}} \times 100 \qquad (2)$$

The extracted sandbox oil was transesterified to obtain sandbox methyl ester (SBME) or generally Fatty acid methyl ester (FAME) as shown in equation 3.3.





Triglyceride Methanol
Glycerol Methyl Esters
(Extracted oil)
(FAME)

Plate 3.2: Extracted sandbox oil undergoing transesterification to obtain sandbox methyl ester and Glycerol

2.4 Physiochemical and thermal properties of the Biodiesel

The physiochemical properties of the sand box seed oil produced were determined following American Society for Testing and Materials (ASTM) methods.

2.4.1 Colour

The colour of the biodiesel produced was determined by observation using several independent competent individuals. Biodiesel colour was correlated using colour charts. The odour was likewise determined.

2.4.2 Moisture content

The moisture content of the biodiesel was obtained by using a known weight of the biodiesel sample put into a clean previously weighted beaker and dried in an oven at 105°C for 4 hours. The sample was taken from the oven, cooled in a dessicator for about 30 minutes and then weighed. The procedure was repeated until a constant weight is obtained. The percentage moisture in the seed was then calculated.

2.4.3 Acid Value

Biodiesel sample of 15g is dissolved in 50ml bioethanol/diethyl ether mixture (1:1 by volume). The sample is treated potentiometrically with alcohol KOH. After each titration, a pH glass electrode that has been specially developed for non-aqueous acid-base titrations is thoroughly rinsed with isopropyl alcohol.

2.4.4 Cloud Point

Manual test methods were adopted to determine the cloud point. 45ml sample was placed in a test tube resting on a cork disk immersed in the cooling bath. The bath temperature is maintained by a mixture of ice. Sample temperature is monitored by a standard thermometer and the test was repeated in increments of 1˚C as the sample cools. At each increment, the test tube was carefully removed, and the sample inspected for the appearance of haziness. The temperature where haziness is detected was reported as the cloud point.

2.4.5 Pour Point

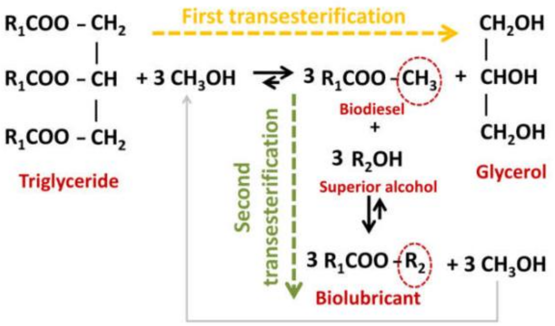
Pour point determination employs the same apparatus and cooling rate as described for cloud point. The sample was tested at 3˚C increments and at each increment the sample was removed from the bath and gently tilted to examine the meniscus. The lowest temperature where the meniscus remains horizontal was reported as the pour point.

2.4.6 Flash Point

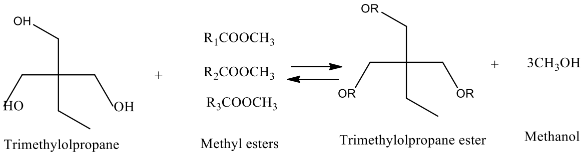
The flash point of the biodiesel produced was determined experimentally by heating the sample in a container and then introducing a small flame just above the sample surface. The temperature at which there was a flash/ignition was recorded as the flash point.

2.5.1. Synthesis of Biolubricant from SBME using trimethylolpropane (TMP)

The synthesis of biolubricant adapted was as described by Surapoj et al. (2013) with slight modifications. The obtained sandbox methyl ester (SBME) or generally Fatty acid methyl ester (FAME) was synthesized with trimethylolpropane (TMP) to obtain trimethylolpropane ester or sandbox oil Biolubricant (SBBL^T) as shown in equation 3.4.



Double transesterification for biolubricant production R1 = alkyl group of fatty acids. R2 =alkyl group of the superior alcohol.



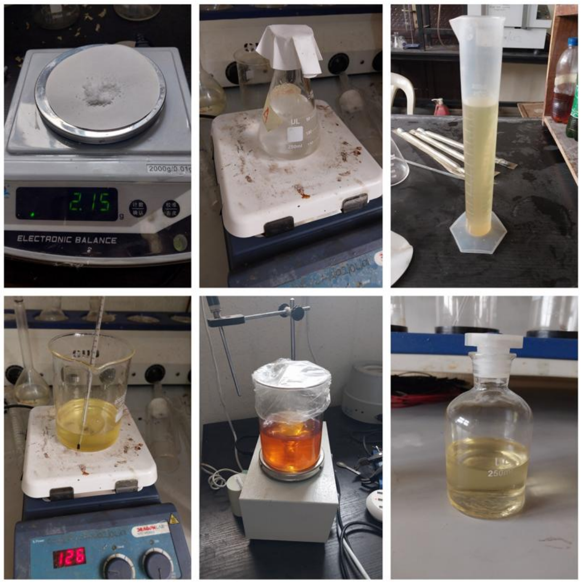


Plate 3.3 Double transesterification for biolubricant production

In this method, trimethylolpropane (TMP) was initially heated using a transesterification experimental set-up. This set-up comprises 50-mL three necked round-bottom flask equipped with a water-cooled reflux condenser, a thermometer, Kipp's apparatus and a thermofisher scientific 50094711 (THERMO SCIENTIFIC CIMAREC I MONO DIRECT) stirrers operated at1000 rpm. The (TMP) contained in the flask was heated to and kept at 110°C for 15 min, at 1000rpm under CO_2 flow. 110°C was maintained to evolve moisture from the TMP. Using the same experimental set-up, a $Ca(OH)_2$ catalyzed batch transesterification reactions between SBME (FAME) and already cooled TMP were conducted at SBME–TMP ratios: 3:1, 4:1, 5:1, 6:1 and 7:1. Each of the stated SBME–TMP ratios was subjected to transesterification at temperatures of 80, 100, 120, 140 and 160 °C. Each of the individual experimental runs at a given particular ratio and temperature was monitored and samples were collected at reaction times intervals of 1, 2, 3, 4 and 5 h for analyses. At the end of each reaction, the product mixture was brought to room temperature and filtered to separate the solid catalyst from the liquid mixture sandbox oil biolubricant (SBBL^{t}). The filtered sandbox bio-based stock was analysed using the GC to determine the product composition. The un-reacted methyl ester was not removed before measuring the properties of the bio based TMP ester to eliminate potential conjugation reaction at destructive high temperature (180–200°C) molecular distillation (needed to remove unreacted methyl ester) involving poly unsaturated fatty acid (PUFA) and also improve wear resistance of the bio based TMP ester (Yunus et al., 2003; Yunus et al., 2004).

2.5.2: Flash point

The cup was filled at any convenient temperature (not more than 560 °C below the expected flash), so that the top of the meniscus is expected at the filling line. The light test flame would be on and adjusted to 3.2 - 4.8mm. The heat was applied initially to the sample to give a change in temperature of 14 – 170 °C per minute. When the sample was about 560 °C below the anticipated flash, the heat source was decreased to the rate of 5 – 60 °C per minute. Starting with at least 280 °C below the flash point, the test flame was also applied when the temperature reached each successive 2 °C mark. The test flame was passed across the centre of the cup at right angles to the diameter and not more than 3mm above the upper edge of the cup in one direction. At the time of the next flame application, it was passed in opposite direction. The time taken to pass the test flame across the cup was about 1 sec. The flash point was recorded as the temperature at which an instantaneous flash occurs on application of the flame.

2.5.3: Viscosity

The viscosity was measured at temperatures of 40 °C and 100 °C. At the start a proper viscometer three (3) spindle was chosen. The sample was transferred to a beaker large enough to hold the viscometer spindle. The beaker was placed on a heating mantle which was set to a desired temperature, while the temperature of the sample was raised. The temperature of the sample was checked using a thermometer. When the desired temperature reached, the sample was then removed from the heat source and the viscosity was read. The spindle was attached to the upper coupling by holding the coupling between the thumb and forefinger while cautiously rotating the spindle counter clockwise. The knob was set to the minimum speed which includes the centipoise range of the material that will be tested. The uppermost number on the knob indicates the revolutions per minute (rpm). The spindle was immersed into the sample up to the middle of the identification in the shaft. The viscometer was turned on and allowed to run until a constant reading (usually 5 to 10 revolutions) was attained. The viscosity of the sample was determined by multiplying the obtained reading with the factor for the spindle divided by speed comb. The viscosity was reported to two decimal place accuracy for viscosities under 100 and to the nearest whole number for viscosities over 100.

2.5.4 Viscosity index

The viscosity index is an empirical number; its value was determined using the value obtained for the viscosities. The viscosities obtained were converted to kinematic viscosities by dividing with their densities from which the viscosity indexes were determined using ISO viscosity grade viscosity index calculator.

Furthermore, the instrumental characterizations of the SBO and the modified products were carried out using the following referenced procedures in Table 2.1.5

Table 3.1.5: Instrumental Analyses and procedures

Analyses	Reference Procedure
GC	ASTM D6584 (2017)
FTIR	ASTM E168 (2016)

III. RESULTS AND DISCUSSION

3.1. Physicochemical properties of SBO and SBO biolubricants

The physicochemical properties of the SBO and the biolubricants produced by transesterification with trimethylolopropane (TMP) are presented in Table 4.1.

Table 3.1: Physicochemical properties of SBO and modified SBSO Biolubricants

Property	units	SBO	SBOBL$_T$	Petro lubricant (Standard)	Methods
Oil yield	%	46.7			AOAC 920.85
Specific gravity	g/ml	0.910	0.990	0.848	ASTM D1217-15
Viscosity @ 40 °C	cSt	25.08	48.53	46.476	ASTM D445
Viscosity @ 100 °C	cSt	6.02	11.65	7.940	ASTM D445
Viscosity index		180	139	105	ASTM D2270
Pour point	°C	18	-11	-20	ASTM D97
Flash point	°C	210	235	220	ASTM D93

Physicochemical properties of vegetable oil and their respective lubricants

Lubricant	Viscosity 40^{o}c (cSt)	Viscosity 100^{o}c (cSt)	Viscosity Index	Pour Point	Flash Point	References
Castor oil	220.6	19.72	220	-27	250	[18]
Castor/TMP	20.94	4.47	127	-	-	[19]
Jotropha OIL	35.4	7.9	205	-6	186	[20]
Jotropha/TMP	43.9	8.71	180	-6	325	[21]
Palm oil	52.4	10.2	186	-5	-	[22]
Palm /TMP	47.9	9.0	176	-2	355	[23]

Olive oil	39.62	8.24	190	-3	318	[24]
Olive /PE	68.08	12.00	190	-24	-	[25]
Repeseed oil	45.60	10.07	180	-12	252	[26]
Repeseed/alcohols	7.8-38.2	2.7-8.4	205-224	-31.3 to -18.9	-	[27]
Soybeen oil	28.86	7.55	246	-9	325	[28]
Soybeen/alcohols	10.3-432.7	3.0-34.4	45-195	-	-	[29]
Sunflower oil	40.05	8.65	206	-12	252	[30]
Sunflower /octanol	7.93	2.74	226	-3	-	[31]

The obtained oil yield of sandbox oil was 46.7 %. This value was higher than the 47.5 % and 49.2 % yields reported for palm kernel by [32]. However, this value was lower than the 59.9 % yield, reported by [33]. This difference in the PKO yields could be attributed to the extraction method used [34].

The specific gravity value of SBO biolubricant SBOBL$_T$ synthesized by transesterification with trimethylolpropane (TMP) (0.990 g/mL), is similar to that of standard biolubricant (0.848g/ml). However, it could be seen from the table that there was increase in the specific gravity when compared to the SG of the raw SBO sample (0.910 g/mL). However, the petroleum lubricant had the least SG value of 0.848 g/mL. The higher SG values of the sandbox oil biolubricant (SBOBL^T), compared to the SBO value, was attributed to increase in molecular complexity resulting from the trimethylolpropane (TMP) backbone [35]. It could be seen that the specific gravity value for the biolubricant samples were higher than the Petro lubricant. This could be attributed to chemical structural change in the constituent molecules. It is worth noting that the specific gravity changes lead to a corresponding change in the mass of the products. In other words, the higher the specific gravity, the heavier and more viscous the lubricant oil would be. Hence, the biolubricant has the advantages of better sustenance at elevated temperature as well as the ability to withstand greater loads. The compatibility of biolubricant products with either the heavy or light duty engines is determined by its SG. This compatibility is the ability of the sample to mix with other liquids [36]. As such, materials with lower SG (<1) floats in water, where as those with higher SG (>1), sink in water. Therefore, biolubricants with higher SG and viscosity, last longer on the applied surfaces and joints [37].

The viscosities of SBSO biolubricants synthesized by transesterification with TMP SBOBL^T were 48.53 cSt at 40 °C and 11.65 cSt at 100 °C, respectively. It can be seen that the viscosity of synthesized biolubricant is much higher than that of Petro lubricant. From the values in Table 4.1: For the SBO sample, its viscosities were lower than the values reported for SBO and sandbox oil, by [27, 28], respectively. However, the SBO sample viscosities were lower than the values reported for Jatropha oil by [38]. These values for SBO biolubricant samples are less than those of biolubricant from SBO reported as 480.63 cSt at 40 °C and 20.54 cSt at 100 °C, by [39]. Also, the values of the viscosities of SBO biolubricants in this work were less than those of biolubricant from Jatropha oil which were reported as 55.17 cSt at 40°C and 10.96 cSt at 100°C, by [40]. The values for SBO biolubricant are comparable with those of petroleum lubricants which were evaluated as 46.476 cSt at 40°C and 6.940 cSt at 100°C, although the viscosities at 100 °C of the SBO biolubricants in this work were greater than that of the petroleum lubricants. As such, the synthesized SBO biolubricants exhibits greater thermal stability and can endure greater mechanical stress than petroleum lubricants.

The viscosity index values for the SBO biolubricant synthesized by transesterification with trimethylolpropane (TMP) SBOBL^T and petroleum lubricant are 139 and 105, respectively. The value for SBOBL is higher, though close to that of the petroleum lubricant value. Viscosity index is defined as the property of a liquid that helps to resist changes in viscosity with increases or decreases in temperature. In lubricants, it is important to have higher viscosity index values. This is because lubricants with higher viscosity index significantly resist viscosity changes with changes in temperature. The viscosity index of SBO in this work is 180. This value is slightly lower than 185, reported by [40] for SBO. Also, this value was lower than the 233-viscosity index value for Jatropha oil, reported by [41].

The pour point is defined as the temperature at which the oil solidifies enough to resist flow. The pour point was reduced from 18 °C for SBO to – 11 °C for biolubricant after double transesterification respectively. However, the pour point of the petroleum lubricant is – 20 °C. Hence, these results show that the pour point of the biolubricant and petro-lubricant are good enough to permit their use at low temperatures. This was possible because, in the biolubricants, the products thermal resistance is greatly enhanced, due to the fact that the thermally fragile glycerol in the SBO triglycerides is replaced by the trimethylolpropane backbone and the elongated chain obtained during epoxy ring opening, which are thermally stable. Therefore, the significant thermal stability and cold properties of the SBO biolubricants, compared to the SBO. Similar results were obtained by [42] for the synthesis of biolubricant using SBO; as well as by [43], for the synthesis of biodiesel from SBO.

Flash point of a fuel can be defined as the temperature at which the fuel can ignite when exposed to a heat source. This is of importance when safe handling, storage and transportation are involved [44]. The flash points of SBO and palm kernel biolubricants samples SBOBL^T were 210 °C and 235 °C respectively. Thus, the products are categorized as non-hazardous products due to their high flash point values. With respect to lubricants, flash point of a lubricant is the temperature at which some vapour is emitted from the lubricant to temporarily ignite a flame. Flash point is a very important property that must be considered in evaluating the overall flammability hazard of a biolubricant, as well as other similar materials. On the other hand, the flash point of the petroleum lubricant was 220 °C. The obtained results were similar to those reported by [45] (>210) and (>300), for SBO biolubricant. These flash point values of the obtained SBO biolubricants samples were also in the range of those reported by [46] for Need biolubricant (262 °C) and [43] Jatropha biolubricant (274 °C).

3.2 Fourier Transform Infrared (FTIR) analyses of SBO and SBO biolubricants

The surface chemistry of the extracted oil SBO sample and the synthesized biolubricants were analyzed using FTIR spectroscopy in other to determine the functional groups present in them. The results in Figs. 4.1 – 4.2 were analyzed and likened with known signature of identified materials in the FTIR library [47]. For all the samples, the main peaks of importance would be highlighted and briefly discussed.

For the SBO sample (Fig. 4.1), the peak at 1047.5 cm^{-1}is a characteristic of C – O stretching, an indication of the presence of alcohol and phenol, which are oxygen-containing compounds. Similarly, the peak at 2020.284cm^{-1} is characteristics of combination N–H stretching, combination O– H stretching, indicating the presence of organic compounds. Furthermore, the peaks centred at 3002.457 cm^{-1} and 3289.143 cm^{-1} are characteristic of O – H stretching, indicating the presence of carboxylic acids, which are oxygen-containing compounds and water; as such the easy biodegradability of the oil sample.

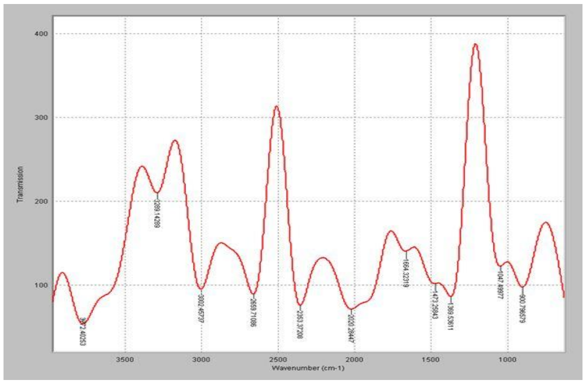


Fig. 3.1: FTIR spectrum of SBOS

Fig. 3.2 shows the FTIR spectrum of synthesized biolubricant to confirm that the transesterification reaction between methyl esters and Trimethylolpropane (TMP) actually occurred. From the spectrum, the peak at 1773.514 cm^{-1}, which falls in the range of carbonyl (C=O) group, indicates the absorption for esters [48]. Similarly, the absorption peaks at 2931 and 2886 cm^{-1}, are within the absorption range for C – H stretching in the hydrocarbon component of the biolubricant. Finally, the broad peak at 3340 cm^{-1}, indicates the presence of O – H groups, which is an indication of the presence of oxygen-containing compounds and water molecules which appear as impurities in the TMP.

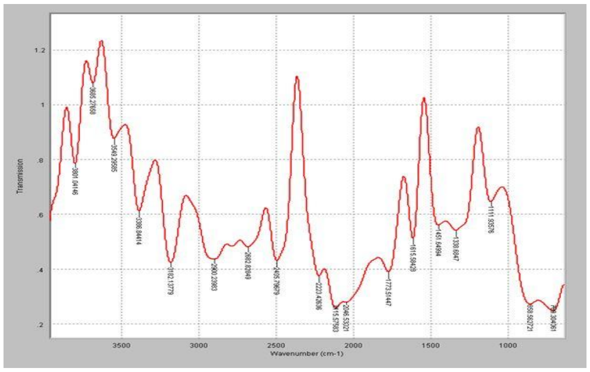


Fig. 3.2: FTIR spectrum of SBOS biolubricant obtained by transesterification of methyl esters and TMP

3.3. Fatty Acid composition of SBOS, and synthesized biolubricant

The fatty acid compositions of sandbox oil (SBO), SBO biolubricant synthesized by transesterification with trimethylolpropane (TMP) ($SBOBL^T$), and SBO biolubricant synthesized by epoxidation-esterification ($SBOBL^E$) methods are presented in Table 4.2. Similarly, the fatty acid profile of SBOS and $SBOBL^T$ is presented in Figs. 4.3 and 4.4, respectively. From the results in the table, it could be seen that the saturated and unsaturated fatty acid compositions of SBOS and $SBOBL^T$ were (72.69 % and 27.31 %), (81.81 % and 18.19%) respectively. This is an indication that the SBOS and $SBOBL^T$ samples were all highly saturated. For the SBO sample, the predominant saturated fatty acid was lauric acid, with 41.85 %. On the other hand, oleic acid was the predominant unsaturated fatty acid, with 17.45 %. Similar fatty acid composition was obtained for SBOS by [49]. However, there is the need to further improve on the saturated level of the SBOS using modification prior to their possible application as biolubricant [50].

From the results presented in Table 4.2, it could be observed that the saturated and unsaturated fatty acid compositions of $SBOBL^T$, were 81.81 % and 18.19 %, respectively. From these results, it could be seen that the percentage compositions of the saturated fatty acids for the $SBOBL^T$ sample, increased while that of the unsaturated decreased after transesterification of the SBO sample using TMP. This could be due to the heat assimilation. This is because as the heating temperature rises, it results in the fatty acids modification. Hence, the saturation level increases due to decreased prevalence of two or three double bonds [51]. Henceforth, this results in the polyunsaturated fatty acids (PUFA) decrease, with corresponding increase in the saturated fatty acids (SFA) [52]. Therefore, transesterification of SBOS using TMP increases its saturation level, making the modified oil more usable as biolubricant. The predominant saturated fatty acid in $SBOBL^T$ sample was lauric acid, with 47.61 %. On the other hand, oleic acid was the predominant unsaturated fatty acid, with 16.11 %. Similar fatty acid composition was obtained for transesterification with trimethylolpropane (TMP) of methyl ester of Jatrophacurcas oil. However, like in the case of the transesterification of methyl ester with trimethylolpropane (TMP), there was increase in the percentage of saturated fatty acids. This was due to the heating, resulting in increase in temperature, associated with epoxidation reaction. This is because of the fact that heat treatment of oils or methyl esters, induces fatty acids modifications with two or three double bonds [53]. These explanations, substantiates the reason for the decrease and increase of the unsaturated fatty acids (USFA) and saturated fatty acids (SFA), respectively [54] The improvements in the stability of the $PKBL^T$; samples were due to increase in SFA samples as evident in the Table 4.2.

Table 3.2: Fatty acid compositions of the SBOS and SBOBL^{T}

Fatty acid	Fatty acid Type	SBOS (%)	SBOBL^{T} (%)
C 8:0 (Caprylic acid)	Saturated	0.11	0.58
C10:0 (Capric acid)	Saturated	5.08	2.13
C12:0 (Lauric acid)	Saturated	41.85	47.61
C14:0 (Myristic acid)	Saturated	18.34	20.42
C16:0 (Palmitic acid)	Saturated	6.13	8.52
C18:0 (Stearic acid)	Saturated	1.18	2.55
C18:1 (Oleic acid)	Unsaturated	17.45	16.11
C18:2 (Linoleic acid)	Unsaturated	9.86	2.08
Saturated fatty acids (%)		72.69	81.81
Unsaturated fatty acid (%)		27.31	18.19
Total (%)		100.00	100.00

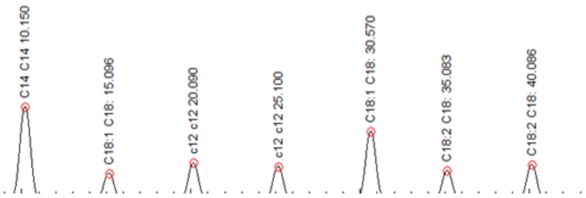


Fig. 3.3: Fatty acid profile of SBOS

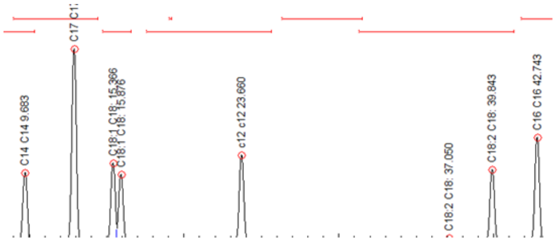


Fig. 3.4:Fatty acid profile of SBOBL^{T}

3.4. Factor sensitivity analyses and kinetics of SBOS extraction

3.4.1. Effect of Time and Particle Size

Feed material properties determine the efficiency of oil extraction process, especially the particle size [55]. Hence, the effect of average particle size on SBOS oil yield was investigated using different particle sizes. Fig. 4.5 shows the effect of particle size on oil yield of SBOS using n-hexane as the extracting solvent with the corresponding Table A1 of appendix A. This shows that the smallest particle sizes of 0.5mm extracted more when compared to its immediately preceding bigger particle size of 1.5 mm. This increase in SBOS yield with particle size decrease could be due to the bigger interfacial area of the solid, thus, intra particle diffusion resistance is less for small particle sizes, due to the shorter diffusion path. On the other hand, intra particle diffusion effect is more evident for bigger particles. As such, it caused appreciable decrease in oil extraction [56]. Nevertheless, the extraction rate would increase, with greater grinding. This is because of increased freed oil from the cells, making it easily available for extraction. As earlier stated, this was due to the increased surface area of the ground SBOS with decreased particle sizes that lead to high rate of oil dissolution from the milled sample into the solvent as well as improved rate of mass transfer resulting from shortened diffusion path [57].

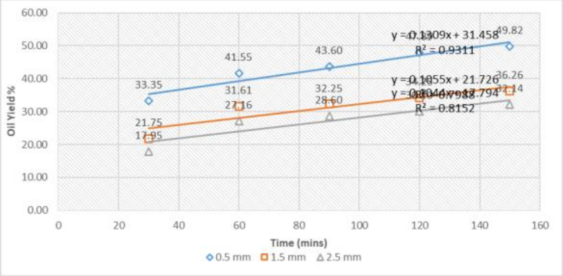


Fig. 3.5: Effect of time and particle size on the yield of SBOSat 55°C

3.4.2. Effect of Temperature and time

The effect of temperature on SBOS yield using n-hexane, at five temperature levels of 35, 45, and 55°C and times of 30, 60, 90, 120 and 150 min at paricle sizes of 0.5 mm is as shown in Fig. 4.6 with the corresponding Table A2 of appendix A. It could be seen from the figure that SBOS yield increased with temperature during the extraction process. This increase was attributed to the enhanced diffusion of the oil as well as reduction in the oil viscosity at elevated temperature [58]. This temperature increases also the mass transfer cofficient of extraction leading to increase in the oil yield

From the Fig. 4.8, it could be seen that the extraction process was fast initially, between 30 and 90 min. However, it steadily reduced between times of 90 to 150 min. This reduction is attributed to internal diffusion, while the fast extraction process at the initial stage was as a result of free oil on the sandbox oil surface which was exposed to fresh solvent. Hence, ease solubility of the SBOS in the solvent, leading to fast oil extraction. In this work, the oil yield of palm kernel increased with both temperature and time, with the highest yield of 49.82 %, obtained at temperature of 55°C and 150 min, for 0.5 mm particle sizes.

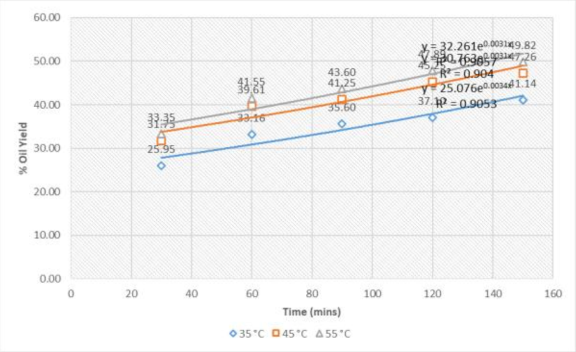


Fig. 3.6: Effect of temperature and time on yield at particle sizes of 0.5 mm

CONCLUSION AND RECOMMENDATIONS

4.1. Conclusion

The following conclusions were drawn from the research carried out. The sandbox seed have a high lipid potential of 46.7%. This oil has good physiochemical and energy characteristics, but it is not recommended for direct use in diesel engines due to its high acidity and density.

1. It has been established that oil extracted from sandbox seed was successfully modified for possible use as biolubricant using transesterification of TMP method.
2. SBO biolubricant samples blend have the viscosity ranges and viscosity indexes that are comparable with mineral lubricant.
3. Characterization results of the modified biolubricant samples indicated that the sample synthesized by transesterification by TMP method had better lubricant properties compared to the Petrolubricant.

4.2. Recommendations

These recommendations are hereby made:

- ❖ Study of the feasibility of the synthesized SBO biolubricants for industrial applications.

- ❖ The methods of SBO biolubricants synthesis used in this research should be encouraged for use in commercial production of biolubricants.

4.3 Contribution to Knowledge

- ❖ This research has successfully applied transesterification of TMP method for the synthesis of SBO, for possible use as biolubricants.

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