

Process Optimization of the Transesterification Processes of Palm Kernel and Soybean Oils for Lube Oil Synthesis

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Abstract

Palm kernel and soybean oils were used as raw materials to produce lube oils. Their transesterification/conversion processes were investigated for different catalyst-oil concentrations. The optimum conditions for obtaining biolubricants with improved properties were found to be close for both oils. For the palm kernel oil, the maximum conversion of the triglyceride to methyl ester was 98 % at an optimum temperature of 56 °C for catalyst concentration of 0.6, 6:1 methanol-oil ratio and lube oil yield of 92 %, while for soybean oil, the conditions for maximum conversion (95%) of the triglyceride in the soybean oil occurred at 60 °C, for 0.5 catalyst concentration and 6:1 methanol-oil ratio with lube oil yield of 88 %. Furthermore, the PKO gave higher biolube oil yield compared to soybean oil. The addition of ethylene glycol coupled with subsequent blending of the oils with mineral oils helped to modify the products of the second transesterification which resulted in the desired lube oils.

Keywords: Bio-lube oil; Catalyst concentration; Conversion; Methyl ester yield; transesterification processes

INTRODUCTION

Despite the renewability and low toxicity advantages of vegetable oils over mineral oils, their high processing costs, lower their market demands [1], hence the need to optimize their parent reactions for improved cost competition. Belafi, et al. [2] produced bio-lube from fuel oil via enzymatic esterification in a solvent-free system. The tribological and physico-chemical properties of the lube oil proved it to be biodegradable and environmentally friendly, although, the enzymatic esterification process was noted to be quite complex and expensive. Transesterification is the reaction between an alcohol (Methanol/ethanol) and triglyceride in the presence of a catalyst for the production of methylester

which can subsequently be converted to lube oil; an alkali catalyst usually makes the reaction faster compared to other catalysts [3]. According to Erhan et al. [4], 85-90 % of the total global lubricants are obtained from non-renewable petroleum precursors /mineral oils. The continuous and conscious exploration of cheaper means of conversion of polyolesters sourced from fatty acids of vegetable oils may result in significant cost reduction of the synthesized lube oil [5]. In the study carried out by Ghazi et. al. [6], the kinetics of the transesterification synthesis of bio-lubricants from jatropha curcas oil was done at varying temperatures and constant pressure. Their findings showed that the highest lube oil yield (i.e. 47 %) was obtained at 200 °C. A good lubricant is characterized by properties such as its ability to resist wear, low freezing point, high viscosity index, thermal stability, specific heat capacity, boiling points and high resistance to oxidation and corrosion. Based on the study of Helwani et al. [7], harnessing the potentials of exploiting green technologies for biodiesel production is a necessity; although, the target product is diesel, the study shows that the stages of biodiesel production can be optimized as a route through which bio-lubes can be produced. A lubricant controls friction for improved efficiency and reduced wear in automobiles and machine parts [8], whereas, bio-diesel serves as fuel for automobiles. The work of Kombe [10] involves the re-esterification of high free fatty acid oils for improved biodiesel yield. Bio-lubes are valuable alternatives to petroleum-sourced lubricants due to their renewable nature and lesser pollution effects with respect to their release of toxic substances. Their fuel properties are somewhat comparable, which corroborates the need to improve on the quality and cost of lube oils synthesized from vegetable oils. In addition, research on the use of biofuels as replacements for fossil fuels has grown significantly because, fossil fuels are known to have high quantity of gaseous emissions which may result in climate change, drought and threat to plant and animal existence [11]. Transesterification reaction is usually between an alcohol (Methanol/ethanol) and triglyceride in the presence

of a catalyst. In a base-catalyzed transesterification process, the FFAs and percent moisture are to be controlled as they result in side-reactions such as hydrolysis and saponification thus, it is therefore recommended that the FFA value be less than 3% in order to allow for maximum conversion. According to Meher et al. [13], increased acidity decreases the efficiency of conversion of TAGs to esters. Oziokwo [14] carried out extraction and characterization of lube oil obtained from soybean oil and the lube oil produced was seen to have similar properties with those of light duty oil (SAE) and heavy duty oil (SAE40) with good flash/fire points in the range of 243 °C-290 °C and 260 °C-300 °C respectively. Patil and Deng [15] carried out a study on biodiesel production from edible and non-edible vegetable oils but the logical effect of food competition with expected hike in the prices of edible oils make them the less preferred of the two oil types. Generally, plant oils with high concentrations of saturated linear fatty acids are undesirable raw materials for lube oil production because, they often appear as solids at room temperature. Research has it that, oleic acid is the most ideal target source component in vegetable oils when considering them for lube oil production hence, this research aims at optimizing the production process of the bio-lubricant synthesis from soybean and palm kernel oil using two stage trans-esterification reactions since the oils are known to possess appreciable quantities of the acid. Some studies claim that the mono-unsaturated fatty acids (e.g. oleic and palmitic acids) found in some plants, make them viable alternatives for producing lubricants and hydraulic oils [16]. Smith et al. [17] highlighted some benefits of biolubricants. According to them, lube oils sourced from petroleum, get their lubricity from additives such as chlorine and sulfur while biolubricants require other special compounds (additives) to improve their properties [18]. The studies by Wan et al. [19, 20] which involved the acid catalysis of the esterification reaction of FFA to FAME for biodiesel production also gives impetus to the subject matter where high methyl ester yields may eventually result in high conversion of the starting material to bio-lube oil.

This paper explores the possibility of exploiting the process optimization of the conversion of triglycerides (TAGs) in palm kernel and soybean oils as routes through which Fatty Acid Methyl Esters (FAME/bio diesel) can be obtained as initiation steps towards producing lube oils.

MATERIALS, EQUIPMENT AND METHODS

The materials, equipment and reagents used are as listed below.

Reagents: Methanol (500 mL) of 99.9 % purity and

manufactured by Sigma-Aldrich Lobal Chemie, 250 mL of 99% pure ethylene glycol (made by Analar), 98 % pure potassium hydroxide (pellets) and 99 % sodium hydroxide (500mL) made by Sigma-Aldrich, 1.0 litre of 99% concentrated sulphuric acid produced by Sigma-Aldrich and 500 mL distilled water of 99 % purity.

Apparatus: beakers (50-200 mL), burette (50mL), density bottle, glass funnel, measuring Cylinder, pipette (25mL), reflux Condenser, retort Stand, tri-neck Round bottom flask, thermometer (limit = 200 °C).

Equipment: Oven Vs-1202d3 (Vision Scientific Co. Ltd., material of construction is steel with powder coating), Calibrated viscometer and viscometer bath - ASTM IP, UBC, Size 4, No: 2118, PSL 1643/13, $c = 0.4959$, Ubbelohde and BS/U viscometer (made in England) SYD-265D-1, LiDA xmT-F 9000), No: 2014 -7-765, 1800W, 220V was used to determine the kinematic viscosities of the samples at two different temperatures; 40 °C and 100 °C. The equipment is coupled with a 50 Hz, 0.12 A, 1250 rpm, 0.5 μ F/450 V YN60-06 motor, The SYD-3536 Cleveland open cup flash and pour point tester was used to test for the flash and pour points of the samples.

Raw Materials Collection

Palm kernel and soybean oils were purchased a week after storage from the Ota main market in Ogun State, Nigeria.

Initial Characterization of the Oils

The oils were characterized in order to determine the properties (i.e. density, pour, flash point, viscosity index, saponification value and free fatty acids of the oils) and their suitability for use as base oils for producing biolubricants.

Experimental Design (MINITAB 15)

Response surface method (RSM) was adopted in carrying out the experimental design (MINITAB 15), in order to evaluate the response/effect some changes (i.e. reaction temperature, methanol to oil ratio and catalyst concentration) would have on the target variable(s) such as lube oil yield etc. The method considers different variables/factors within some specified limits (i.e. maximum and minimum points i.e. HIGH (+) and LOW (-) points for application. Table 1 shows the results obtained for the different run orders and variables considered. Based on the results, the operating conditions for the transesterification reactions as shown in Table 2 were obtained.

Table 1: Table of Standard and run orders

S/N	Std Order	Run Order	Pt Type	Blocks	Reaction Temperature (°C)	Methanol/Oil Mole Ratio	Catalyst Concentration (g)
1	8	1	2	1	60	6	0.8
2	3	2	2	1	48	7	0.6
3	9	3	2	1	54	5	0.4
4	7	4	2	1	48	6	0.8
5	12	5	2	1	54	7	0.8
6	6	6	2	1	60	6	0.4
7	5	7	2	1	48	6	0.4
8	13	8	0	1	54	6	0.6
9	1	9	2	1	48	5	0.6
10	14	10	0	1	54	6	0.6
11	2	11	2	1	60	5	0.6
12	10	12	2	1	54	7	0.4
13	11	13	2	1	54	5	0.8
14	15	14	0	1	54	6	0.6
15	4	15	2	1	60	7	0.6

Table 2: Response surface design conditions for the operating parameters/factors

Factors	Parameter	Maximum	Minimum
A	Reaction Temperature (°C)	60	48
B	Methanol/Oil Mole Ratio	0.7	0.5
C	Catalyst Concentration (g)	0.8	0.4

Procedure

Oil Esterification for FFA Conversion

In order to curb the risk of exposing the oils to saponification, the free fatty acids (FFAs) in the oils were reduced by reacting the oils with methanol in the presence of sulphuric acid as catalyst; 100 g each, of the oil samples, were weighed and transferred into two separate three-neck round bottom flasks. 20 % w/w methanol and 5 % w/w H₂SO₄ were also weighed and mixed in a conical flask. The methanol-acid mixture and the oil samples were placed in a water bath whose temperature was raised to 65 °C. To each round bottom flask, a mechanical

stirrer was inserted through one of the necks while the other necks were stoppered by stirrers rotating at 750 rpm. The bath temperature was maintained at 65 °C for homogeneity. After sixty minutes, each sample was withdrawn with a picking pipette and titrated against 0.1 M solution of KOH in order to determine the FFA content of the oil. The titration was carried out for 240 mins and at 60 mins interval. The FFA value was then calculated using (1).

$$\% \text{ Free Fatty Acid} = \frac{(\text{volume of titrant})(\text{molarity of titrant}) * 28.8}{\text{weight} * 100} \quad (1)$$

Transesterification

The process synthesis of the bio-lubricants involved a two stage transesterification so as to reduce the FFAs in the oils to appreciable limit; the first stage was aimed at producing an intermediate product (methyl-ester) from both oils, while the second involved the conversion of the methyl-esters formed to produce the polyol esters of the oils as shown below:

Methyl ester (biodiesel) synthesis

100 g each, of soybean and palm kernel oil samples were transesterified with methanol using KOH as catalyst. The weight ratio of oil-to-methanol was varied from 3:1 to 10:1, and the time of the experiment, was in the range of 60 to 120 mins while maintaining a constant catalyst weight of 5 % w/w of oil and a fixed temperature of 60 °C in order to account for the yield of the methyl ester produced.

Polyol ester (bio-lubricant) Synthesis

The methyl esters obtained from both oils were reacted with ethylene glycol in 50 mL batches using 0.5 M Sodium methoxide (prepared simply by dissolving fresh clean sodium in 30 % methanol) as catalyst; this was so as to bring about the second stage transesterification. Based on the results from RSM i.e. Table 2, the weight ratio of oil-to-methanol used was 3.5:1, the amount of catalyst used was 0.8 % w/w of the total reactants and the reaction temperature was 120 °C which was maintained for two hours thirty minutes (2.5 h).

Preparation of Lube oil blends

Two different blends of the bio-lube oils obtained were prepared by mixing 30 % (135 mL) of each synthesized poly ester obtained with 70 % mineral base oil (315mL) to make up 450mL blend for each of both products from soy bean and palm kernel oils. The lube oil blends were prepared in order to improve their lubricating properties.

Bio-lube Characterization

All four bio-lube oil samples (i.e. two synthesized oils without blends and two blended biolubricants obtained from both oils) were characterized for each production phase in order to determine the lube oil densities, their pour points, flash points, viscosity indices, saponification values, iodine values and their viscosities. The properties were determined as follows:

i. Density

An empty beaker was weighed and the weight (w_1) was recorded. 50 cm³ each, of the produced lube oils was then measured using a measuring cylinder and poured into the beaker and weighed again; the weight w_2 was also noted. The densities of each of the lube oils were determined by dividing the difference in weights w_1 and w_2 of the lube oils by the known volume (50 cm³) of the oil; see Equation (2).

$$\text{Density} = \text{mass/volume} \quad (2)$$

ii. Pour point

The pour points of the produced oils (blended and unblended oils) were measured using ASTM D 97. The pour points of the oils were determined by placing a test jar filled with each of the processed oils in a cooler (water bath) and successive measurements were taken at 30 °C interval until the oils stopped flowing.

iii. Oil Viscosities

The viscosities of the oils were measured at two different temperatures, say 40 °C and 100 °C respectively. At the start, a

proper viscometer spindle, say spindle 3 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 adjusted to the desired temperature and the samples responded to the changes in temperature. The temperature of each sample was checked using a thermometer. As soon as the desired temperature was reached, each sample was removed from the heat source and its viscosity was recorded. The spindle was then attached to the upper coupling by holding the coupling between the thumb and forefinger while cautiously rotating the spindle anticlockwise. The knob was set to the minimum speed (rpm) with the spindle immersed into the sample up to the middle of the shaft. The viscometer was then turned on and allowed to run until a constant reading (usually 5 to 10 revolutions) was attained. The viscosity of the sample was then determined using (3). The viscosities were recorded to 3 significant figures for viscosities less than 100 and to the nearest whole number for viscosities over 100.

$$\mu = \nu \times \theta \quad (3)$$

Where:

μ = value on spindle

θ = reading obtained (factor for the spindle-speed combination)

iv. Viscosity index

The lube oil viscosities obtained in iii were converted to kinematic viscosities by dividing through with their densities; the viscosity indices of the oils were then determined using the ISO viscosity grade index calculator.

v. Saponification value

2 g of each oil sample was weighed and poured into a 250 mL conical flask. 50 cm³ of 0.5 ethanolic KOH was added to the sample. The mixture was then heated to saponify the oil. The unreacted ethanolic KOH was then back-titrated with 0.5 M HCl using 2-3 drops of phenolphthalein as indicator. Saponification values of each of the oil samples were calculated from (4).

$$\text{Saponification Value} = \frac{Z \times M \times 56.1}{W} \quad (4)$$

Weight of oil taken (W): 1.0 g

Strength of the acid (M): 0.1 M

The values recorded are as given below:

The difference (Z) between the titre value (T_{R2}) of HCl against KOH alone after reflux and the titre value (T_{R1}) of HCl against

oil and KOH after reflux = 2.7 mL

Titre Value of HCl against KOH alone after reflux (T_{R2}) = 48.9 mL

Titre value of HCl against oil and KOH after reflux (T_{R1}) = 46.2 mL

vi. Flash point

The cup of the flash point tester was filled with each sample to a convenient temperature (i.e. about 56 °C below the expected flash), so that the top of the meniscus rests at the filling line. The light test flame which came on was adjusted to 3.2 - 4.8 mm. The heat was applied initially to the sample to give a change in temperature of 14 – 17 °C per minute. When the sample was about 56 °C below the anticipated flash, the heat source temperature was adjusted to 5 – 6 °C per minute. Beginning with at least 28 °C below the flash point, the test flame was applied when the temperature reached each successive 2 °C mark. The test flame was passed across the center of the cup at right angles to the cup diameter and not more than 3 mm above the upper edge of the cup in one direction. At the time of the next flame application, it was passed in opposite direction and 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 was seen as soon as the flame and oil were in contact.

vii. Temperature effect on viscosity

The viscosities of the synthesized lubricant and biolubricant blend samples were determined at temperatures of 30, 40, 50,

60, 70, 80, 90 and 100 °C. At first, spindle 3 was selected; the samples were then transferred to separate 250 mL beakers. The contents of the beakers were heated and constantly mixed by means of a heating mantle. The spindle was then immersed into the sample up to the middle of the indentation in the shaft. Each sample was attached to the upper coupling by holding the coupling between the thumb and forefinger while cautiously rotating the spindle anticlockwise. The viscometer was turned on and allowed to run until a constant reading was attained; this was taken as the viscosity of the sample.

RESULTS AND DISCUSSION

Methyl Ester From PKO

Table 3 gives methyl ester yield as obtained from the PKO. During the experiments, a total of 15 runs were carried out. The catalyst used relative to oil (i.e. methanol to oil ratio) was varied between 5:1 – 7:1 respectively for different catalyst concentrations and at three different temperatures 48, 54 and 60 °C as shown in Table 3. It is evident that at 60 °C, the highest methyl ester yield was obtained when the catalyst concentration and methanol to oil ratio were 0.4 and 6:1 respectively. This implies that for maximum results, methanol concentration should be kept at 0.4 when the reaction temperature is 60 °C. When the reaction temperature was 54 °C, the methanol – oil ratio that gave the highest yield was 6:1 and for a catalyst concentration of 0.6. As soon as the reaction temperature was maintained at 48 °C, the methanol - oil ratio of 7:1 gave the highest yield at that temperature.

Table 3: PKO methyl ester yield with temperature, catalyst concentration and methanol-oil ratio

Reaction Temp °C	Methanol/Oil Mole Ratio	Catalyst concentration	Yield
60	6	0.8	93
48	7	0.6	97
54	5	0.4	96
48	6	0.8	93
54	7	0.8	95
60	6	0.4	94
48	6	0.4	95
54	6	0.6	98
48	5	0.6	85
54	6	0.6	94
60	5	0.6	92
54	7	0.4	94
54	5	0.8	88
54	6	0.6	93
60	7	0.6	93

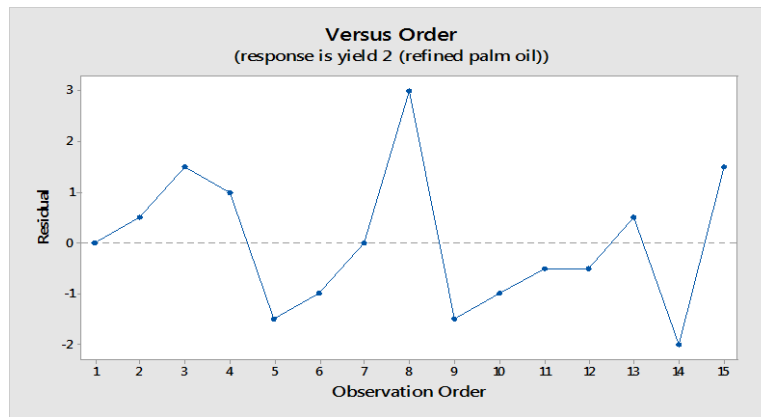


Figure 1: Weighted residual vs observation order

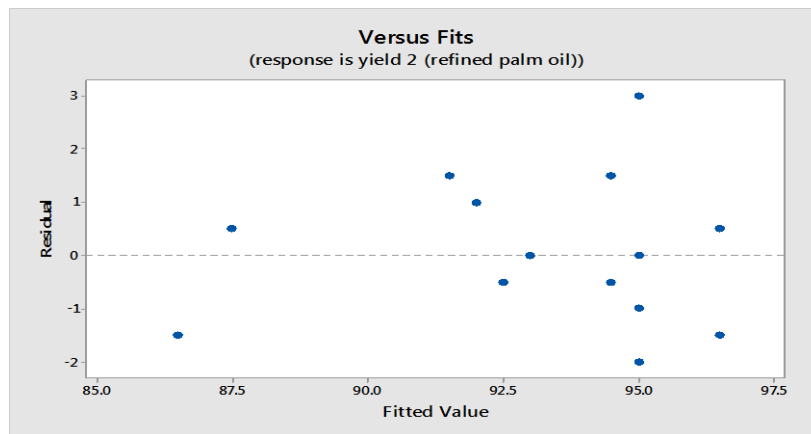


Figure 2: Weighted residuals vs expected yield

In Figure 1, the weighted residuals or expected error was in the range of ± 2 to 3 for all 15 runs. The highest expected yield is about 96.5 but from the experiments, the highest yield recorded was 98 which is an indication of good experimental design. Figure 2 is an illustration of the weighted residual values and the expected yields for the experiments performed while Figure 3 shows the percentage yield expected for the weighted residuals i.e. within the expected error margin or deviation of ± 2 to 3 %; see also Figure 4 which is a contour plot of yield for the different methanol - oil ratios and catalyst concentrations.

The plot further displays what was observed experimentally. For a yield greater than 95 %, the methanol to oil ratio must be > 5.5 . The optimum reaction temperature required for maximum yield is 56 °C for a catalyst concentration of 0.6 with methanol to oil ratio of 6. This implies that lowering the concentration of the catalyst below 0.6 slows down the esterification process but increasing the catalyst concentration lowers the activation energy of the reactants until it gets to 0.6 where equilibrium is achieved i.e. the rate of forward reaction equals the reaction rate in the reverse direction.

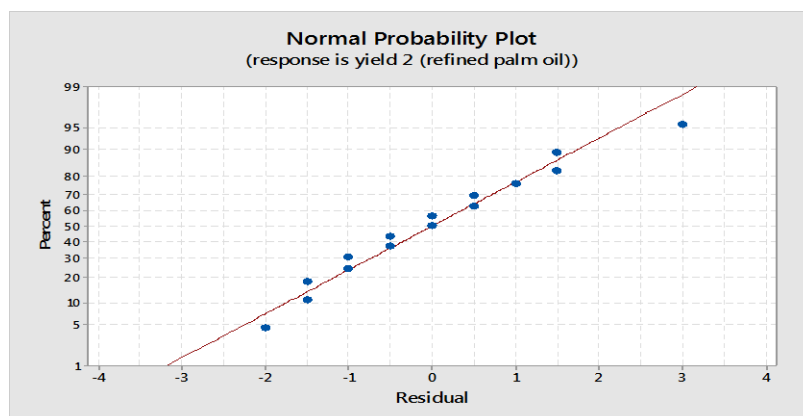


Figure 3: Normal probability plot of Yield vs weighted residual error for PKO measurements

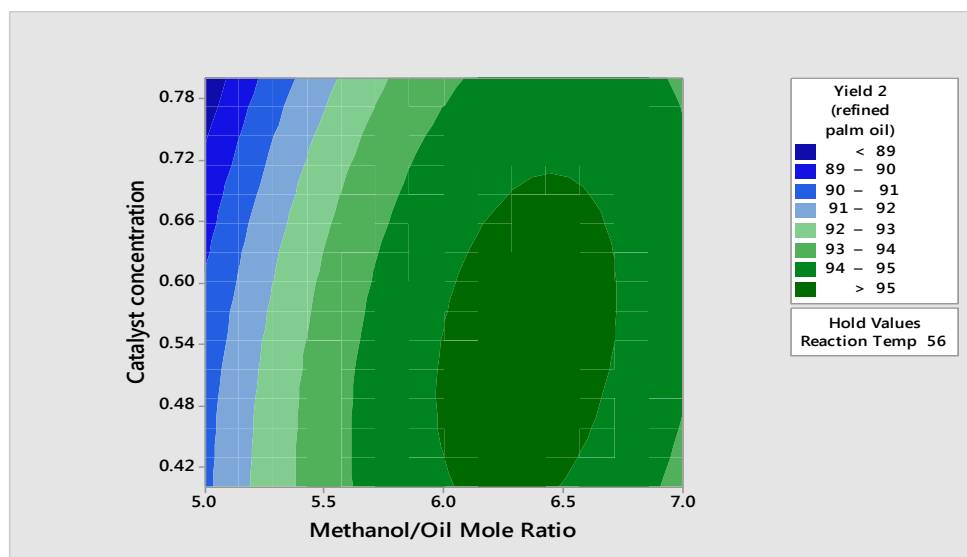


Figure 4: PKO methyl ester yield vs catalyst concentration and methanol-oil ratio

For PKO, with higher catalyst concentration than 0.6, there would be excess catalyst which will result in the catalyst spreading through the reactor thus impeding the interactions between the methanol and palm kernel oil in the forward direction thus, favoring backward reaction which results in less methyl ester recovery due to methyl ester reconversion to triglyceride. At lower than 0.6 catalyst concentration, the yield is less than 94% provided the reaction temperature is greater than 50 °C; see Figure 5. This is because, an increase in temperature increases the rate of conversion of the triglyceride to methylester whereas at lower temperatures, the yield is

expected to drop because the rate of reaction between the methanol and the oil is slowed down. At the onset of the reaction, the conversion of the triglyceride increases with temperature until it approaches the optimum value where the rate of conversion of the triglyceride is maximized hence, the yield is highest/maximum because the reaction tends to approach completion. However, further increase in temperature beyond the optimum value 54 °C causes a decrease in yield as the reaction approaches completion.

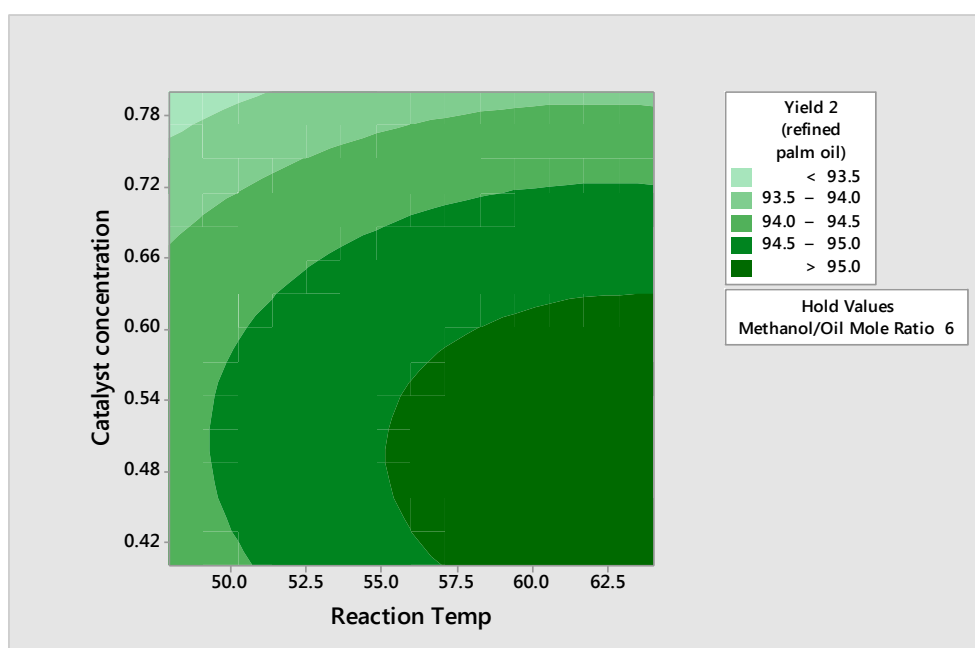


Figure 5: Palm kernel oil methyl ester yield vs Catalyst concentration and Temperature

From the surface plot in Figure 6a, it is clear that the yield is > 94 % for catalyst concentration of 0.6 and methanol-oil ratio of 6:1 when the reaction temperature is 56 °C; the actual value is 98 % which is shown in Table 1. Figure 6b is an illustration of the variation of PKO yield with reaction temperature and

catalyst concentration for methanol-oil ratio of 6:1 while Figure 6c shows the variation of PKO methyl ester yield with catalyst concentration and reaction temperature for constant methanol oil ratio of 6:1.

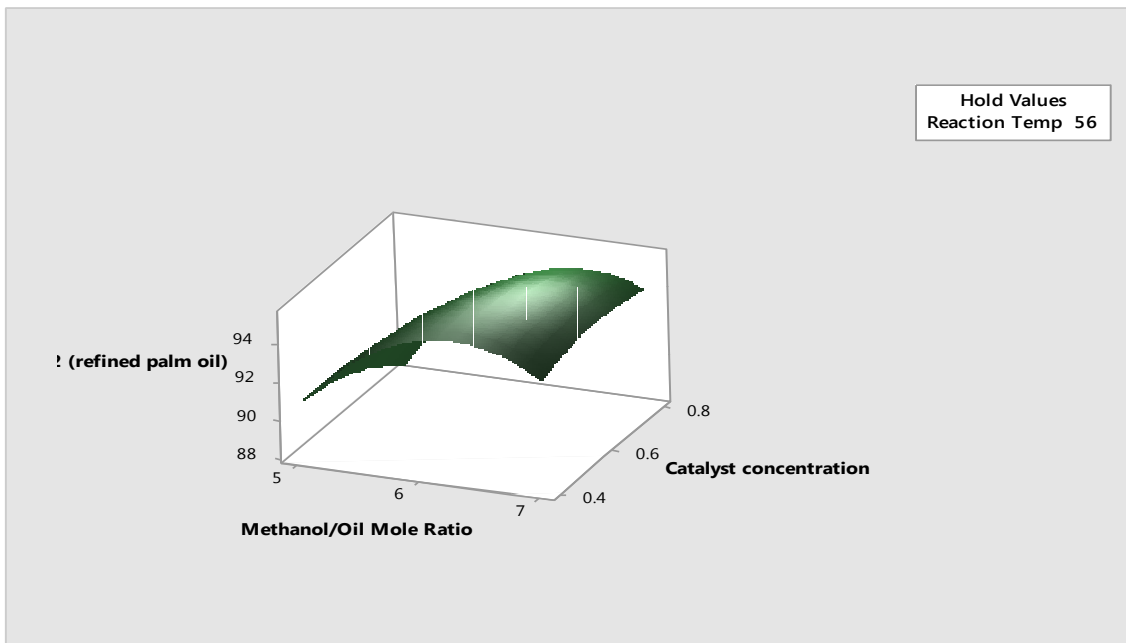


Figure 6a: PKO methyl ester yield vs methanol-oil ratio and catalyst concentration

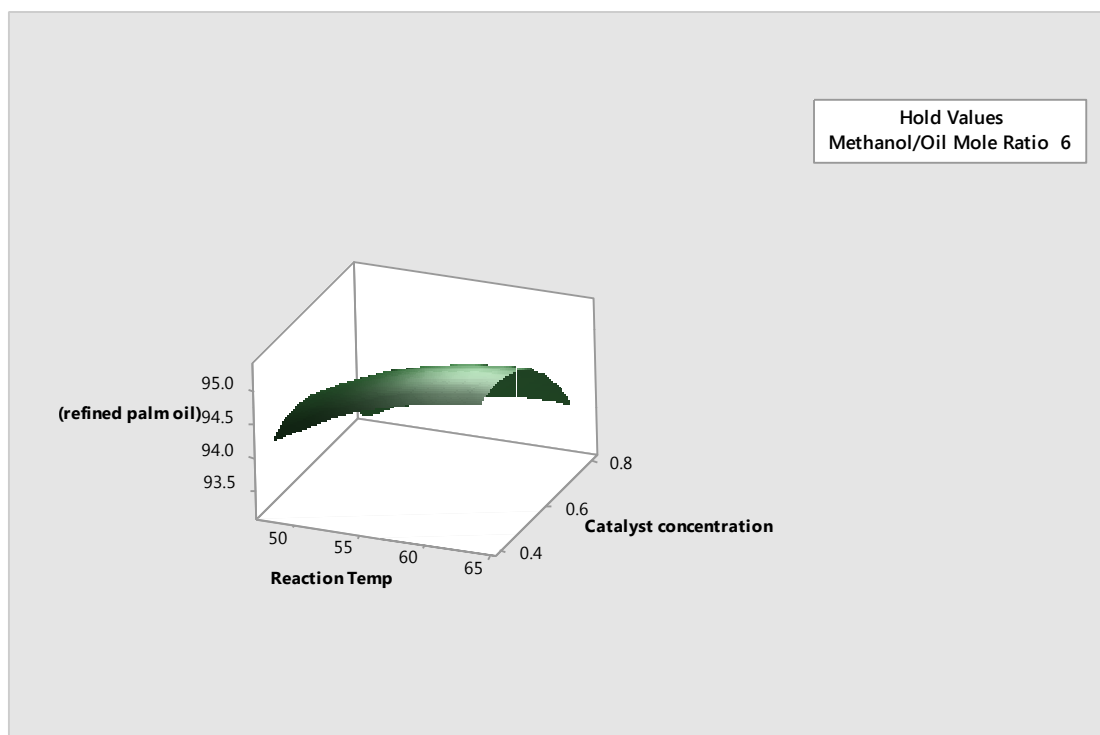


Figure 6b: PKO methyl ester yield vs temperature and catalyst concentration

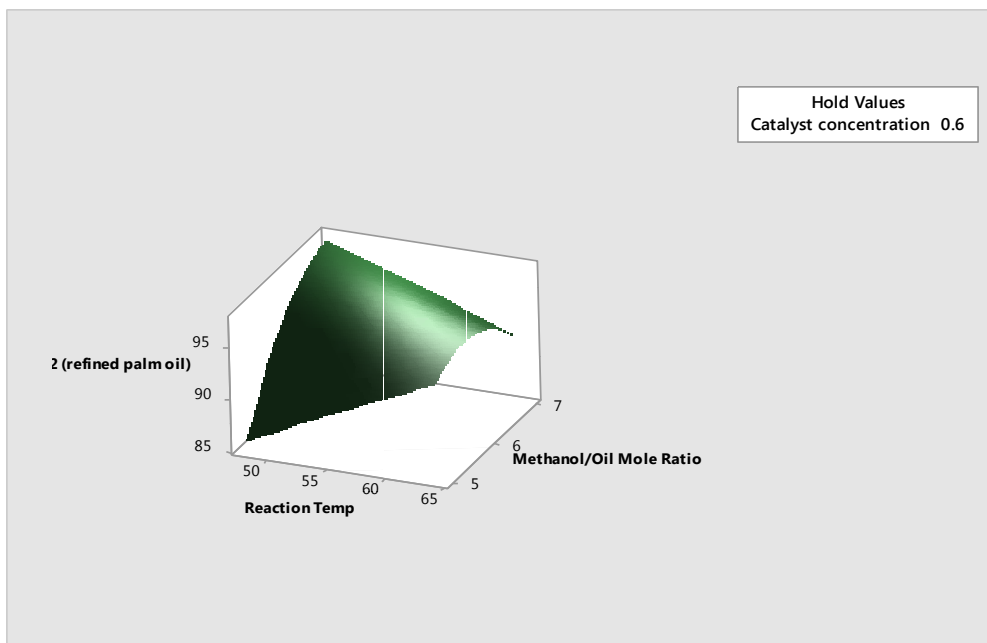


Figure 6c: surface plot of palm kernel oil methyl ester temperature vs methanol/oil ratio

Methyl Ester From Soybean

Table 4: Soybean oil methyl ester yield at different reaction conditions

Reaction Temp °C	Methanol/Oil Mole Ratio	Catalyst concentration	Yield
60	6:1	0.8	94
48	7:1	0.6	87
60	6:1	0.4	95
48	6:1	0.8	89
54	7:1	0.8	90
60	6:1	0.4	91
48	6:1	0.4	89
54	6:1	0.6	88
48	5:1	0.6	86
54	6:1	0.6	94
60	5:1	0.6	92
54	7:1	0.4	94
54	5:1	0.8	88
54	6:1	0.6	93
60	7:1	0.6	84

In Table 4, the conversion of the soybean oil was between 92-95 % when the reaction temperature, methanol-soybean oil ratio and catalyst concentration were 60 °C, 0.4 and 6:1

respectively. For an increase in the concentration of the catalyst; the highest possible conversion recorded was 95 % considering other temperatures, catalyst concentrations and

methanol-soybean oil ratio. This implies that, for optimum results, the reaction conditions must be kept at the stated conditions for maximum conversion of the soybean oil. At 60 °C, for higher than 0.4 catalyst concentration, the yield obtained is less than 95 % because, the activation energy of the reaction instead of being lowered is increased by the presence of excess catalyst which slows down the reaction rate and hence increases the resistance to reaction which subsequently affects the degree of conversion of the triglycerides in the soybean oil. With one of the three variables (catalyst concentration, methanol-oil ratio

and temperature) kept constant while varying the other two parameters, it can be seen that the optimum conditions for producing the highest yield of lube oil from soybean oil must be at a temperature of 60 °C, methanol-oil ratio of 6:1 and catalyst concentration of 0.4 since other conditions gave yields < 95 %. Figure 7 gives an illustration of the variation of methyl ester yield with catalyst concentration and methanol-oil ratio.

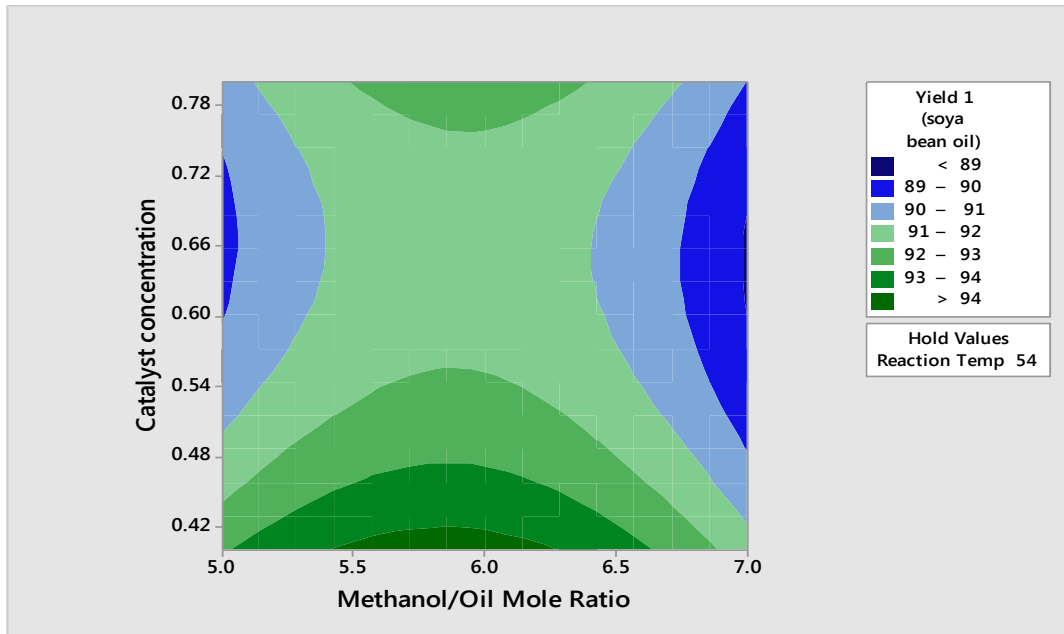
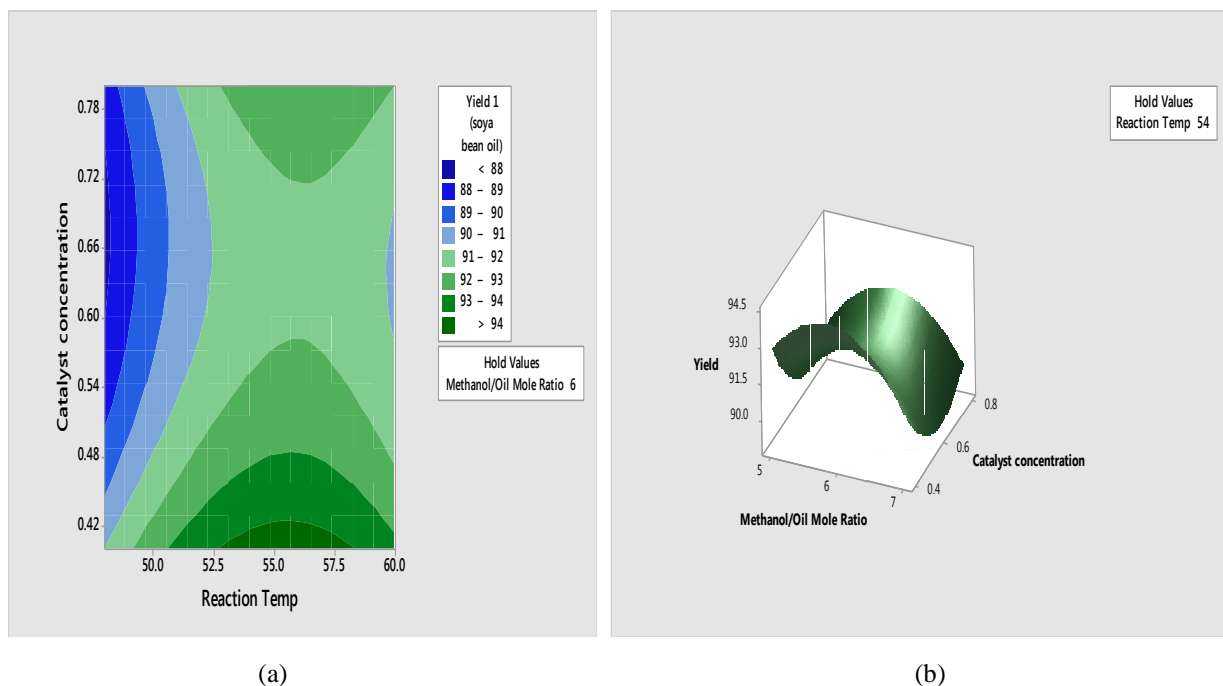


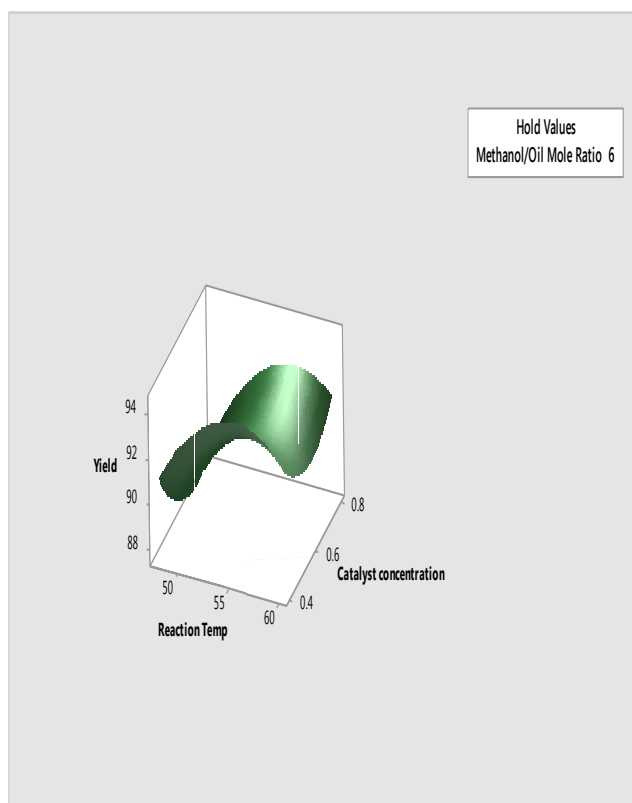
Figure 7: Soybean oil methyl ester yield vs catalyst concentration and methanol-oil ratio



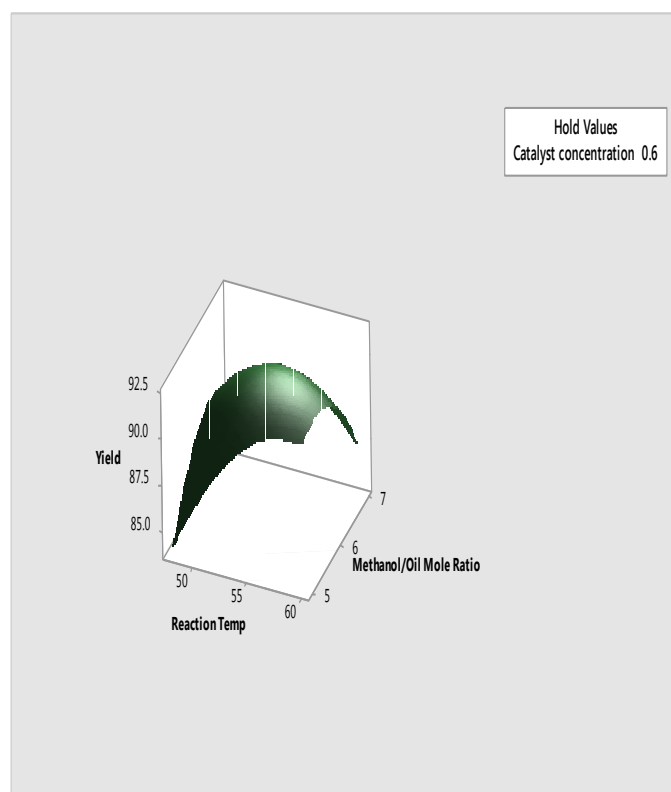
(a)

(b)

Figure 8a: Soybean oil yield vs catalyst weight and temperature; **8b:** Soybean oil methyl ester yield vs methanol-oil ratio and catalyst weight



(c)



(d)

Figure 8c: Soybean oil yield vs temperature and catalyst weight; **8d:** Soybean oil yield vs temperature and methanol-oil ratio

In Figure 8a, it is evident that in order to obtain high methyl ester yield of > 94 % from soybean oil which subsequently translates to higher conversion to bio-lube, the reaction temperature must be maintained between 53 and 58 °C and the catalyst concentration must be less than 0.42 while Figure 8b shows what happens when the reaction temperature is kept at 54 °C for different catalyst concentrations and methanol-oil ratio. The maximum yield is 94.5 % given by methanol-oil ratio of 6:1 and 7:1 for catalyst concentration of 0.6 and 0.4 respectively. The results show that in order to maximize the methyl ester yield from soybean oil at 54 °C, one of the following must be done to the other two parameters (catalyst concentration and methanol-oil ratio); decrease in the catalyst concentration and increase the volume of the methanol from 6 to 7 times the volume of the soybean oil so that the rate of reaction increases with a corresponding decrease in the catalyst concentration for improved yield and vice versa; see Figures 8c and 8d.

Physicochemical Properties of the Raw Oils and Their Lube Oil Blends

Physicochemical Properties of the raw oils

The physical properties (densities, saponification values, iodine values, specific gravities and acid values) of the vegetable oils were compared with standard properties of the oils from literature and the results are shown in Tables 5 and 6. The results show that the oils were still good for use when the sample oil properties were compared with properties of standard oils; see *Bio-lube characterization*. The values tabulated are average values obtained from 3 tests per property. The apparatus and reagents used could have caused the slight difference in values, although, the values lie within the acceptable range for quality vegetable oils of these types (PKO and soybean oils). Also, the method of extraction and exposure of the oils to oxidants could have resulted in the slight variations in the measured properties. The acid values are indicative of the quality of the oil samples i.e. They are within the acceptable range for both oils at the time the experiment was performed.

Table 5: Physicochemical properties of standard soybean oil and the soybean oil

Physicochemical Properties	Soybean oil Standard	Soybean oil used
Density	0.921±0.16	0.9
Saponification value (mg KOH/g)	193.63±1.81	194.67
Free Fatty (FFA) (mg KOH/g)	1.36±0.08	1.05
Iodine value (mg KOH/g)	15.86±4.02	17.34
Specific Gravity value (S.G)	0.918±0.06	0.9
Acid value (mg KOH/g)	2.72±0.3	2.1
Viscosity index	95	95

Table 6: Physicochemical properties of standard Palm Kernel oil and the PKO

Physicochemical Properties	P.K.O Standard	P.K.O Used
Density	0.921±0.1	0.912
Saponification value (mg KOH/g)	280.5±56.1	306.81
Free Fatty (FFA) (mg KOH/g)	1.35±0.15	1.29
Iodine value (mg KOH/g)	15.86±4.02	16.68
Specific Gravity value (S.G)	0.904±0.6	0.912
Acid value (mg KOH/g)	2.7±0.3	2.58
Viscosity index	95	95

Table 7 shows the physicochemical properties of the oils. The densities of the synthesized oils are lower than those of the crude oils because of the reactions and conversion/reduction reactions leading to conversion of the triglycerides of the oils to methyl esters. The viscosity at 40 °C for soybean oil, was higher than that of palm kernel oil because, even in their raw forms, soybean oil offers higher resistance to flow relative to palm kernel oil at that temperature; the same is seen for the oil viscosities at 100 °C. Due to the corresponding higher

viscosities of the crude and raw soybean oils relative to those of palm kernel oils, soybean oils gave higher flash points since soybean oil will require more heat to raise its temperature to its vapour state for ignition. For the pour points of the oils, soybean oil being denser than palm kernel oil will become semi-solid at -9 or -15 °C for the raw and synthesized soybean oils respectively, while it is higher for the crude and synthesized palm kernel oil. The synthesized biolubricants were found to have relatively similar densities.

Physiochemical Properties of the Lube oil blends (Synthesized oils)

Table 7: Pyhsico-chemical properties of crude vegetable oils and synthesized bioluricants

Sample Properties	Soybean Oil		Palm Kernel Oil	
	Crude	Bio-lube	Crude	Bio-lube
Specific Density (mg/ml) @ 20 ⁰ C	0.917	0.86	0.9120	0.868
Kinematic Viscosity at 40 ⁰ C (mm/s ²)	33	27.643	31.42	25.315
Kinematic Viscosity at 100 ⁰ C (mm/s ²)	8.05	4.643	7.71	4.315
Flash Point (°C)	342	305	243	215
Pour Point (°C)	-9	-15	22	9.01
Specific Gravity	0.918	0.86	0.904	0.868

Table 8: Physico-chemical properties of synthesized biolubricants and their blends

Sample Properties	Soybean Oil		Palm Kernel Oil	
	Biolube with additives	Bio-lube Without Additives	Biolube with additives	Bio-lube Without Additives
Specific Density (mg/ml)	0.886	0.86	0.884	0.868
Kinematic Viscosity at 40 ⁰ C (mm/s ²)	78.67	27.643	83.76	25.315
Viscosity at 100 ⁰ C (mm/s ²)	12.84	4.643	14.93	4.315
Flash Point (°C)	312	305	303	215
Pour Point (°C)	-21	-15	9.01	-9

For the different lube oil blends all properties of the soybean and palm kernel oils were enhanced by the additive used; see Table 8. However, it is crucial to consider blending additives with vegetable oils as the viscosities of the palm kernel lube oils improved better than those of soybean lube oils at both temperatures; this then implies that, the additive must have a polymeric similar behavior with palm kernel oil better than the soybean oil i.e. oil properties can be improved by merely adding additives of similar origin and this is the functional

strength of viscosity improvers.

Also, the densities of the lubricants decreased when compared with that of their unrefined samples. This may be attributed to the series of modifications they underwent during the esterification and transesterification processes. The pour points of the synthesized biolubricants significantly improved when compared to those of their vegetable crude oils because of the presence of the polyol groups present in the ethylene glycol during the polyol synthesis and the absence of beta-hydrogen

in the final biolubricant produced. The produced biolubricant was subjected to performance requirement since several applications require specific lube oil properties. These properties include pour point, flash point, viscosity and viscosity index. Synthetic esters normally possess superior thermal stability and low-temperature properties compared to those of the raw oils. Table 8 gives similar observations in the physico-chemical properties of synthesized biolubricant and their blends as seen in [6]. The blend was formulated using 70% mineral base oil (SN500) and 30 % synthesized biolubricant. The pour points of the synthesized biolubricants were significantly improved when compared to those of their vegetable crude oils. The same was observed when the synthesized lubricants were blended with 70% mineral-base oil (SN500) which has a high degree of saturation tendency. This might be due to the effects of the unsaturated fatty acid chains and also due to the absence of beta-hydrogen when the methyl ester reacted with Ethylene glycol.

The flash points of the synthesized biolubricant blends were found to be relatively lower than those of the synthesized biolubes. This is due to the higher flash point value of mineral oil (280 °C) used. Biolubricants are widely used in automotive gear

and transmission applications. Requirements for such applications are high viscosities, high viscosity indices and pour points. Biolubricants have certain advantages owing to the polarity of their ester molecules. The strong dipole movement causes them to be attracted to each other hence, lowering their volatilities and the vapour pressures. Their dipole-mobility helps to attach them to the oxide layer of a metal during lubrication thus preventing corrosion/wear.

Engine Performance of Biolubes

Based on the performance tests conducted on the bio-lube blends, it is clear from Table 9 that, the soybean oil with lower yield gave better performance compared to PKO in terms of all other properties except for TBN number and dispersancy i.e. the ability of the oil to flow/spread on a surface. Based on the engine performance tests conducted, both oil blends gave high oxidative stabilities (see the acid values obtained in the Appendix section, and, rust inhibition/corrosion inhibition, thermal stabilities and antifoam characteristics which are also evident in their low saponification values as presented in Tables 5 and 6).

Table 9: Performance tests for PKO & Soybean oil bio-lubes

Test	Performance of bio-lube oil from PKO	Performance of bio-lube oil from Soybean oil
Anti-rust	Good performance	Good performance
TBN	Better than that of soybean oil Low (ability to neutralize the) acidic products of combustion)	Low (ability to neutralize the acidic products of combustion)
Dispersancy	Good performance	Fairly good performance
Antifoam	Slightly below the minimum detergency performance requirements of API CD & MIL-L-2104 C specifications	Slightly below the minimum detergency performance requirements of API CD & MIL-L-2104 C specifications
Thermal stability	Fairly lower than the limit (i.e. <240 °C for mineral based lube oils)	High thermal stability (i.e. can withstand temperatures >240 °C)
Oxidation stability	High; obvious in the acid value	High; obvious in the acid value
Water separation	Good water separation	Good water separation
Additive depletion	minimal	Minimal

FTIR Analysis For Palm Kernel And Soybean Oils

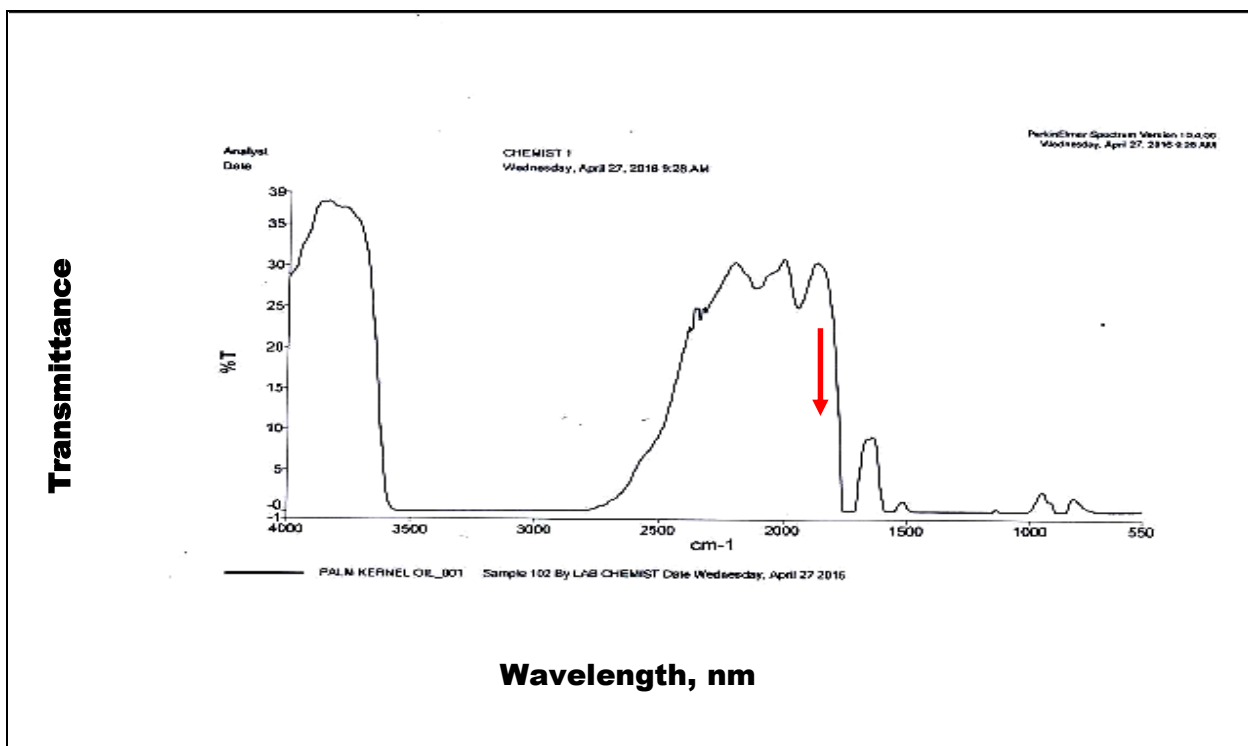


Figure 9a: FTIR spectrum analysis of for ethylene glycol in palm kernel oil

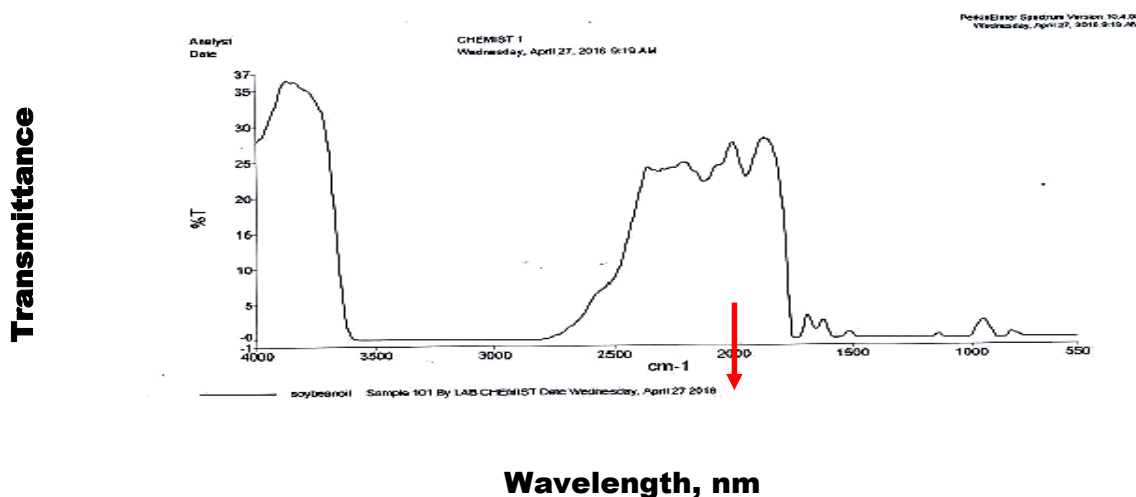


Figure 9b: FTIR spectrum analysis of for ethylene glycol in soybean oil

The infrared radiation spectrum gives a plot of light transmittance against wave lengths of the oil blends. In Figures 9a and 9b, the peaks show that there is low transmittance, and hence high absorption by both oils. The horizontal axes represent wave lengths which increase to the left. Areas that do not have peaks show that photons are not being absorbed at

those frequencies, thus indicating that, the specific bond at that frequency does not exist in the molecule. In Figures 9a and b, the IR spectrum are broken into five zones. Zone 1 extends from about 3700 – 3200 cm^{-1} which indicates the presence of alcohols and phenols (stretch free hydroxyl O-H group from 3700-3610 cm^{-1} ; stretch free hydrogen bonded O-H group), and

1^0 and 2^0 amines or amides (N-H stretch bonds from 3400-3250 cm^{-1}), terminal alkyne C---C-H: C-H bonds from 3300-3270 cm^{-1} . The alcohol peak is usually broad and wide and can be distinguished easily. The more concentrated the solution is with O-H molecules, the more likely it is to form hydrogen bonds since it is easier to stretch hydrogen bonds because, the oxygen atoms pull away the electrons where less energy is required making the peaks appear broader. Alkyne C-H bonds have strong peaks around 3300 cm^{-1} mark. The peak band at 3380.36 cm^{-1} mark in zone 1 appears to be O-H bonds of alcohol due to the broadness of the peak with percentage peak area of 24.38 %. This is in conformity with trimethylolpropane with two functional groups (i.e. alkanes and alcohol functional groups).

In zone 2 (i.e. the region within 3000-2695 cm^{-1}), absorption by alkane C-H bonds, aryl and vinyl C-H bonds, aldehyde C-H bonds, and carboxylic acid C-H bonds occurred because the bonds were identified. The sp^3 C-H bond peak is usually found near-right of the 3000 cm^{-1} mark. The sp^2 C-H bonds can be distinguished because they are located slightly to the left of 3000 cm^{-1} mark. The C-H bonds identified gave many peaks. Evidence of the presence of aldehydes (H-C—O; within 2830-2695 cm^{-1}) and alkanes (C-H; within 3000-2850 cm^{-1}) appear within the 2700-2900 cm^{-1} mark. The carboxylic acid O-H bond appears as a wide, broad peak in the spectrum. The peak band at the 2938.65 cm^{-1} mark in zone 2 appears to be C-H bonds of sp^3 (alkanes) since it is located to the right of the 3000 cm^{-1} mark with percentage peak area of 21.47 %. However, absence of peak band from 2700 – 2900 cm^{-1} mark and broadness peak in the zone proves the non-existence of sp^2 C-H and carboxylic acid O-H bonds. This is indicative of the presence of alkane groups of the trimethylolpropanes in both oils. Zone 3 extends from 2300 – 2100 cm^{-1} which indicates the presence of nitriles C---N stretch bonds and alkynes (C---C stretch bonds). Here, the absorption of alkyne triple bonds and nitrile triple bonds are suspected. These peaks are variable in intensity. The peak band at the 2213.33 cm^{-1} mark in zone 3 appears to be nitrile bonds although, the percentage peak area was very small (3.08 %). Zone 4 shows absorption peaks by carbonyl double bonds. These peaks are usually very strong and intense. They indicate the presence of carbonyls, carboxylic acids, esters, saturated aliphatic compounds, aldehydes, α , β -unsaturated esters, ketones, α , β unsaturated aldehydes, alkenes and possibly 1^0 amines and aromatics; all within the wavelength of 1760-1600 cm^{-1} . In zone 5, the absorption peaks seen were indicative of alkene double bonds and aromatic carbon-carbon bonds. Usually, benzene has two peaks which fall within the 1400-1600 cm^{-1} mark. It can be seen from Figures 9a and b, that there is no existence of peak bands at zones 4 and 5; the only functional groups present are the alkanes and alcohols.

CONCLUSION

Biolubricants with improved properties were synthesized from soybean and palm kernel oils. Esterification reactions of both sample oils showed that, higher conversion of the triglycerides in PKO were obtained relative to the conversion obtained in soybean oil. The temperature of the process affects the yield as well as the inherent properties of the bio-lubes. Both biolubricants had comparable viscosities when compared to those of standard mineral oils after blending. The pour points were also observed to reduce when the synthesized bio-lubes were blended with additives. The results show that the optimum temperature, methanol to oil ratio, catalyst concentration for obtaining higher lube oil yield from PKO are 54 °C, 6:1, 0.6 giving methyl ester yield of 98 %. However, based on the findings, it therefore shows that, at the same temperature, with methanol-oil ratio of 5:1 and catalyst concentration of 0.8, the yield is lowest i.e. 88 % wt/wt of PKO while for soybean oil, the highest lube oil was obtained for methyl ester yield of 95 % at the optimum temperature of 60 °C, for methanol to oil ratio of 6:1 and catalyst concentration of 0.4 respectively and the minimum yield (88 %) was obtained at 54 °C, methanol-oil ratio of 6:1 and catalyst concentration of 0.6. Based on the conditions specified by the experimental design, for the second stage transesterification, PKO gave lube oil yield of about 92 % at a reaction temperature of 120 °C, at a total time of 2.5 hours for catalyst weight-oil ratio of 6:1 and catalyst concentration of 0.6 while the second stage transesterification of methyl ester in soybean oil for 0.4 catalyst concentration, methanol-oil ratio of 6:1, gave lube oil yield of about 88.3 %. Considering the results obtained and that from the RSM used in designing the experiment as shown in Table 2, it then implies that the optimum conditions for maximizing lube oil yield lie between the maximum and minimum operating conditions specified. Furthermore, further work can be done in order to source a way of improving the alkalinity of the lube oils for better cleaning/neutralization of the acidic products of combustion without severely altering the inherent properties of the bio-lube oils; again, this can be done at the transesterification stage. Also, the transesterification process helped to improve on the oxidative stability of the oils as both oils gave lower acid values i.e. 0.21 for PKO and 0.26 approximately for the soybean oil for 10 g each of the methylesters used from both oils. This implies that the transesterification process helped to reduce but improve the acid values of the raw oils used by approximately 90%.

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