

Production of ecofriendly bio-lubricant samples from palm kernel oil using different chemical modification approaches

¹Samuel O. Egbuna ¹Ukeh J. Nwachukwu ²Chinedu M. Agu * ¹Christain O. Asadu ²Bernard Okolo

¹ Chemical Engineering Department, Enugu State University of Science and Technology, Enugu, Nigeria.

² Chemical Engineering Department, Michael Okpara University of Agriculture, Umudike, Nigeria.

*Corresponding author: eduetal@yahoo.com

ABSTRACT

This work focused on the chemical synthesis and characterization of palm kernel oil (PKO) for bio-lubricant production using transesterification of palm kernel methyl ester (PKME) with trimethylolpropane (TMP) and epoxidation-esterification methods. The PKO was extracted using solvent extraction method. The physicochemical characteristics of the PKO and produced bio-lubricant samples were determined using standard methods. Fourier Transform Infrared (FTIR) spectrometry and Gas Chromatographic analyses, were respectively, used to determine the predominant functional groups and fatty acids of PKO and the produced bio-lubricant samples. At 55 °C, 150 min and 0.5 mm particle size, kernel oil yield was 49.82 % (by weight). The viscosities at 40 °C, 100 °C, viscosity index, pour and flash points of the bio-lubricants produced by transesterification of TMP (PKBL_T) and epoxidation-esterification (PKBL_E) methods, were [42.53 cSt, 10.65 cSt, 139, - 11 °C, 235 °C] and [44.69 cSt, 11.42 cSt, 132, - 12 °C, 240 °C], respectively. Time, mole ratio and temperature effects were the main factors that significantly influenced the transesterification and epoxidation processes. The obtained physicochemical properties of PKBL_E and PKBL_T samples showed conformity with ISO VG 32 standard, hence, their possible application as bio-lubricant basestock.

Keywords: Bio-lubricant; palm kernel; Transesterification; Trimethylolpropane; Epoxidation-esterification.

1. Introduction

Globally, the crude oil reserves have significantly drooped, due to its high consumption, as well as the slow natural mineral deposit formation. There is therefore possible impeding energy crisis if not quickly addressed [1]. In order to avert this, scientist and researchers have therefore sought for alternative energy sources using bio-based oil materials. As such, alternative oil sources for chemical process industries, which are renewable, biodegradable,

as well as eco-friendly, are currently being researched. Mostly, vegetable oils obtained from seeds and nuts are often used as a suitable substitute to mineral oil obtained from petroleum [2]. There is therefore need for the development/modification of the vegetable oils into industrial products like biodiesel [3], biolubricants [4], transformer fluid [2], as well as other vital fuels that could be used as replacement for conventional mineral base fuels/fluids.

In Nigeria, due to the availability of huge crude oil reserves, as well as the production, exploration, and refining of petroleum into products like, petrol, kerosene, diesel, our interest is on the production of petrochemical products like bio-lubricants. This is because of the environmental friendliness of the bio-lubricants, when compared to its petroleum base counterpart [4].

In the recent past, researchers have successfully synthesized bio-lubricants from different vegetable oil sources for use as environmentally friendly lubricant. Some of these include but not limited to *Jatropha curcas* oil [4], palm kernel oil [1], palm oil [5], Fluted Pumpkin Seed oil [6], and castor bean biodiesel [7]. It is on this premises that this project seeks to synthesize bio-lubricant from palm kernel oil using different process routes, in other to evaluate the method with better lubricant properties.

Palm kernel oil (PKO) is edible oil that is obtained from the kernel of palm fruit, otherwise scientifically known as *Elaeis guineensis* [8-9]. It is yellowish in color and the tree plant (palm tree) originates from tropical Africa and some part of Asia [8]. Palm kernels are essential by-products obtained during the palm oil milling and processing. It is about 45 to 48 % (by weight) of the palm nut of the *Elaeis guineensis* fruit. The oil yield of palm kernel is about 47 to 59 % by weight [9-10]. The predominant fatty acid in palm kernel oil is lauric acid, with about 48 % of the fatty acid composition of the oil. It also contains myristic acid and oleic acid at 16 % and 15 % compositions, respectively [9,11]. Due to the relatively high

oil yield of PKO, a number of studies be carried out on its utilization for the production of biodiesel [12], as well as in bio-lubricant production [1].

It is as a result of the foregoing, that the authors extend this present study to the use of PKO (because of its high oil yield, availability, as well as bio-degradability), in bio-lubricant production, using a modified process routes, for the purpose of comparison, since limited or no studies by authors, have been channeled towards this direction.

Previously, a good number of studies have been reported on bio-lubricant production using vegetable oils, for potential use as alternative to mineral base lubricant, using the two stage transesterification and epoxidation-esterification methods. In case of two stage transesterification using methanol (using alkali catalyst) and subsequently trimethylolpropane, have been extensively reported in the literature. For instance, Heikal et al. [13], Menkiti et al. [4], Yunus et al. [14], da Silva et al. [7] and Shote et al. [15], successfully used this approach for the production of bio-lubricants using palm oil, jatropha curcas oil, palm-based methyl ester, castor bean biodiesel, and palm kernel oil, respectively. In this method, the main drawback of straight alkali catalyzed transesterification stage, without initial esterification pretreatment stage, is its low alkyl ester yield, as well as product separation difficulty, due to formation of soap [2]. As such, in this work, successive two-step conversion process: an acid-catalyzed esterification (aimed at lowering the FFA content), followed by the alkali-catalyzed transesterification (aimed at improving the alkyl ester yield and purity), prior to the final stage of transesterification with trimethylolpropane, was chosen. The essence is to eliminate these short-coming and ensure higher high grade bio-lubricant with high purity level and yield [4].

For the epoxidation-esterification procedure, the method is often considered because of its advantage of better thermo-oxidative stability, as well as the associated low temperature

properties of the final product [2]. Epoxidation reaction is the reaction of the double bonds and peracetic acid to produce epoxy ring [2,16]. In this work, it is worth mentioning that instead of using the PKO, the obtained alkyl ester from the alkali catalyzed transesterification, was reacted with the peracetic acid to get the desired epoxy methyl ester. This decision is based on the improved thermo-oxidative stability and lower pour point of the final desired product [2,16]. Within the authors' knowledge disposal, there is no existing published work that compares bio-lubricants produced from PKO using these two approaches. Though, several works have reported the production of bio-lubricant from PKO using transesterification with trimethylolpropane [1,14,17].

Therefore, this study focuses on bio-lubricant production from PKO, using alkali-catalyzed transesterification, followed by transesterification with trimethylolpropane and transesterification-epoxidation-esterification methods. The qualities of the produced bio-lubricants were evaluated on the basis of the two methods used, and on the referenced standards. Furthermore, the physicochemical properties of the PKO and the PKO bio-lubricants samples produced were evaluated using standard procedures. Also, the prevalent functional groups, and the fatty acid compositions of the PKO and the PKO bio-lubricant samples, were determined using Fourier Transform Infrared (FTIR), and Gas Chromatography, respectively.

2. Materials and methods

2.1. Materials

Palm kernels were obtained from Aguneze, Ahiazu-Mbaise, in Imo State. Trimethylolpropane was purchased from Sigma Aldrich, Germany. Methanol, sulphuric acid (H_2SO_4), orto-phosphoric (H_3PO_4) and analytical grade n-hexane were purchased from Conraws, Presidential Road, Enugu. The reagents had purity levels of above 99 %, and they were used without further purification.

2.2. Extraction of PKO

Oil extraction from the milled palm kernel oil sample was carried out according to Association of Official Analytical Chemists (AOAC) 963.15 method [18], using soxhlet extractor unit for the five different average particle sizes (0.5, 1.0, 1.5, 2.0, and 2.5 mm). Soxhlet extractor was chosen in order to enhance the solubility of the palm kernel sample in the chosen solvents used. Milled kernels of a particular average particle size (15 g) 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 (Hanna HI-9063), while the time was measured using a stop watch. The oil yield was calculated (see equation 3.1) using AOAC method no. 920.85 at the end of each extraction cycle (30, 60, 90, 120, and 150 min). 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). Similarly, the extraction times were 30, 60, 90, 120 and 150 min. 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 3.1.

$$\% \text{ Oil yield} = \frac{\text{weight of oil extracted (g)}}{\text{weight of sample (g)}} \times 100 \quad (1)$$

The extracted oil sample was palm kernel oil (PKO).

2.3. Physicochemical properties of PKO and PKO bio-lubricant samples

The oil yield (AOAC 920.85) was determined according to AOAC approved techniques [18]. On the other hand, viscosity index (ASTM D2270), viscosity (ASTM D445) and specific gravity (ASTM D1217 – 15), were determined using ASTM standard methods. Also, the pour and flash points were determined using ASTM D97 and ASTM D93 standard methods, respectively. Each physicochemical property was measured three times, and the average values of the properties were determined and noted.

2.4. Fatty acid composition of PKO and PKO bio-lubricants samples

Fatty acid profile was evaluated in line with the AOAC 996.06 (1990). In this procedure, a gas chromatograph (GC) (Shimadzu GC-14B, Model 910), was used to determine quantitatively, the prevalent fatty acids in the PKO and PKBL samples. According to the equipment, a HP 88 capillary column (0.25 mm i.d. \times 100 m, film thickness 0.25 μ m – Shimadzu Corporation, Tokyo, Japan), was used to equip the GC's flame ionization detector and integrator. This was achieved by using 250 °C temperatures for both the injector and detector. However, the oven temperature was retained at 190 °C for a period of 15 min. Thereafter, this temperature was then increased intermittently, up to 230 °C, at the rate of 5 °C per min. Afterwards it was maintained at this temperature for the same time interval as the initial step. The carrier gas used was nitrogen, and was maintained at a pressure of 500 kPa. Finally, the prevalent fatty acids were identified and compared with standard compounds; while the quantity of each fatty acid was calculated from the percentage area of the individual fatty acid [19]. The analysis was carried out three times.

2.5. Transesterification experiment

2.5.1. Synthesis of Palm kernel methyl ester

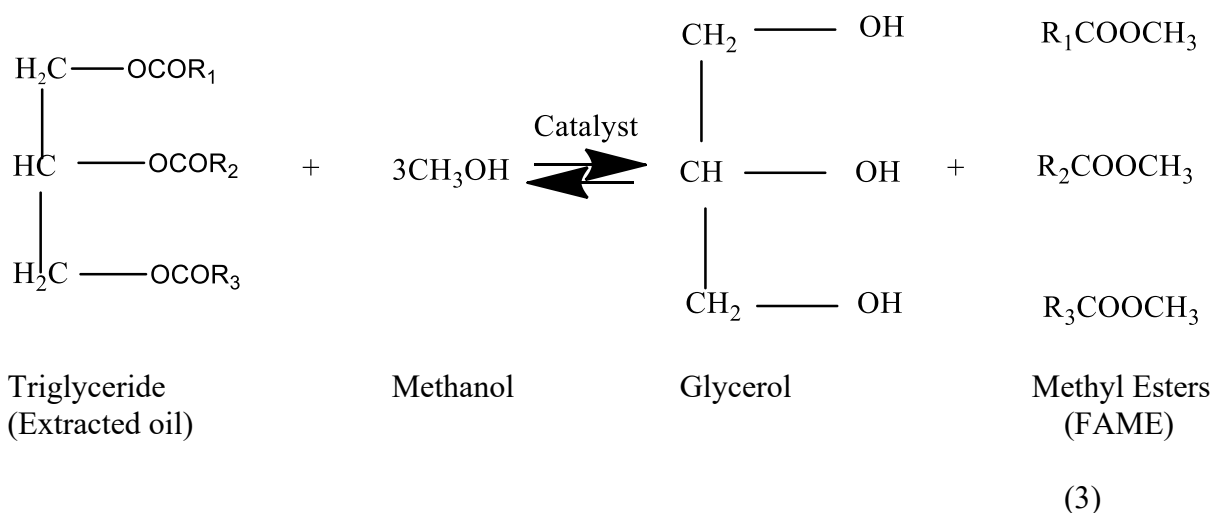
25 ml of each of the palm kernel oil (Triglyceride) sample was poured into 250 ml conical flasks and heated to 60 °C using a water bath. Solution batches of potassium methoxide were

prepared by dissolving 5.1 g (30 wt. %) of KOH pellets in an agitated 250 ml beaker containing 150 ml anhydrous methanol. The potassium methoxide solution was then transferred into warm 25 ml palm kernel oil (triglyceride) sample at a methanol to oil ratio of 6:1. The solution was then stirred strongly, using magnetic stirrer at 500 revolutions per minute (RPM) for 120 min. In order to ensure proper settling, the mixture was left undisturbed in a separating funnel for 24 hrs. At ending of the settling process, the upper layer (methyl ester sample) was poured into a beaker and afterwards properly washed with distilled water. This was aimed at removing unreacted methanol, catalyst, glycerin, soap and other impurities. The demulsification of the fatty acid methyl ester (FAME) sample was then carried out by heating slowly to constant temperature of 100 °C. Finally, the lower layer that consists of glycerol and soap was collected via the bottom of the funnel.

The percentage methyl ester yield of the palm kernel oil sample was calculated using the relationship in equation 2:

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

The product of the transesterification of the extracted palm kernel oil is the palm kernel methyl ester (PKME), or generally referred to as fatty acid methyl ester (FAME); see equation 3.

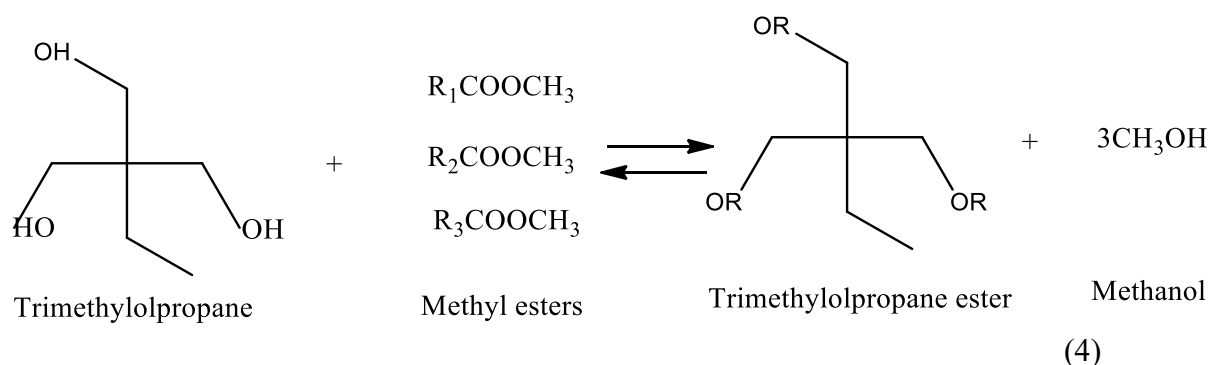


On the other hand, in the present method, FAME of PKO was also obtained using this procedure. Here, a mixture comprising of 300 g of palm kernel oil (Triglyceride), 100 g of methanol, as well as 1% wt/wt orthophosphoric acid catalyst were decanted into continuously stirred reactor. This reactor was that was equipped with a water-cooled reflux condenser to ensure complete reaction. Thereafter, the mixture was then heated to 65 °C and maintained at this temperature for 1hr 30min. After the reaction, the mixture was dosed with 0.2 molar solution of sodium trioxocarbonate IV. This was to ensure complete neutralization of the acid, and eventually stop the reaction. The mixture was then poured into a separating funnel and subsequently allowed to stand for 24 hrs. This was to ensure complete separation of methyl esters and glycerol phases. Glycerol phase at the bottom was emptied into a clean container and allowed to stand. The PKME (FAME) was then heated to 65 °C, so as to ensure the removal of the residual methanol. Finally, the remaining catalyst in the PKME was removed by successively rinsing with hot distilled water at 80 °C. Thereafter, the remaining water in the PKME was eliminated by oven-heating at 100 °C [4].

2.5.2. Synthesis of Bio-lubricant from PKME using trimethylolpropane (TMP)

The synthesis of biolubricant adapted was as described by Surapoj et al. [20] with slight modifications. The obtained palm kernel methyl ester (PKME) or generally Fatty acid methyl

ester (FAME) was synthesized with trimethylolpropane (TMP) to obtain trimethylolpropane ester or palm kernel biolubricat (PKBL_T) as shown in equation 4.



Here, trimethylolpropane (TMP) was initially heated using a transesterification experimental set-up. This set-up comprises of 50 mL three necked round-bottom flask that are fitted to a water-cooled reflux condenser, a thermometer, Kipp's apparatus and a stirrer operated at 1000 rpm. At 1000 rpm, and under the flow of CO₂, the TMP in the flask was heated to 110 °C, and maintained at this temperature for 15 min, before allowing cooling. In order to ensure the evolution of moisture from the TMP, the temperature was maintained at 110 °C. Thereafter, a Ca(OH)₂ catalyzed batch transesterification reactions between PKME (FAME) and already cooled TMP were conducted at PKME–TMP ratios: 3:1, 4:1, 5:1, 6:1 and 7:1, using the same experimental set-up. At 80, 100, 120, 140 and 160 °C, each of the stated PKME–TMP ratios was subjected to transesterification. At intervals of 1, 2, 3, 4, and 5 h, samples from the respective individual runs of the experiment (at a particular mole ratio and temperature) were monitored, collected and analyzed. After every reaction, the mixture was allowed to cool to room temperature, prior to carrying out filtration process, so as to separate the residual solid catalyst from the liquid mixture, which is the palm kernel biolubricat (PKBL_T). The filtered palm kernel bio-based stock was analyzed using the GC to determine the product composition. Furthermore, prior to the characterization of the biobased TMP ester, unreacted methyl ester was not expunged. This was aimed at the improvement of the

wear resistance of the biobased TMP ester, as well as to prevent conjugation reaction that occurs at elevated temperatures (180 – 200 °C), which involves poly unsaturated fatty acid (PUFA) [14,21].

2.5.3. Synthesis of Biolubricant from PKME using epoxidation-esterification reaction

Fifty (50) g of the palm kernel methyl ester sample was placed in three-necked flasks. 7 g of acetic acid was placed in the round bottom flask, followed by the addition of 0.02 g (1.5 wt. %) of H₂SO₄ to the flasks. The mixtures were stirred continuously, followed by the addition of 15 g (1.5 moles) of hydrogen peroxide (15 wt. %). The mixture was added to the flask containing 7 g acetic acid to produce peracetic acid (PAA). The methyl ester sample in the three-necked flask was then heated to 70 °C, followed by the addition of PAA mixtures. These were allowed to react at 70 °C for 7 hours with continuous stirring at 1,200 rpm. Samples were taken out every 1 hour from each of the reaction set up for FTIR analysis to determine the effect of reaction time on the yields (i.e changes in functional groups as the reaction proceeds) at 70 °C. At the end of the reaction, 3 ml of the epoxy methyl ester sample was then removed two times using diethyl ether (2 x 20 ml) in separating funnels. The organic phases (oily layer) of samples were purified (washed) three times with 5% saturated sodium bicarbonate NaHCO₃ (3 x 15 ml) to neutralize the unreacted acid present. Thereafter, organic phase of sample was also washed three times with saturated solutions of sodium chloride NaCl (3 x 15 ml) to obtain epoxy methyl ester of the sample. The sample was dried over anhydrous magnesium sulphate. The solvent (diethyl ether) was then removed using a rotary evaporator. The epoxy oxygen (oxirane) content and iodine value (IV) of the sample was measured according to procedure described by Arumugam et al. [22] and Arumugam and Sriram [23].

The obtained epoxy methyl ester sample was epoxy methyl ester (oxirane) of palm kernel oil (EMPKO^o). Fig. 1 shows the reaction scheme for the epoxidation reaction of PKME to obtain EMPKO^o.

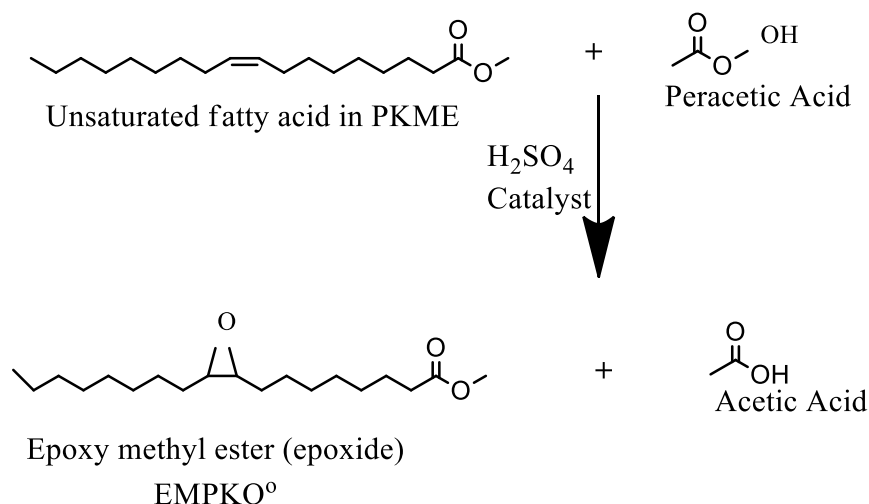


Fig. 1: Reaction Scheme for Epoxidation Reaction of PKME to obtain EMPKO^o [24].

Esterification ring opening reaction

Twenty (20) g of epoxy methyl esters (oxirane) sample (EMPKO^o) was placed in a round bottom flask. 10 ml of ethyl acetate was added to the flask. Each of the mixtures was stirred continuously and followed by the addition of 4 g of acid anhydride. The flask were purged with nitrogen (to exclude air) and followed by the addition of 1ml boron trifluoride diethyletherate to the flask. The epoxy methyl esters (oxirane) sample in the flask was heated to 70 °C. The mixtures were left to react at this temperature for 7 hrs in fume cupboard with continuous stirring. The organic phase (oily layer) of sample was purified three times with 5 % NaHCO₃ (3 x 15 ml) to neutralize the unreacted acid present. Thereafter, organic phase of sample was also washed three times with saturated solutions of sodium chloride NaCl (3 x 15 ml) to obtain the branched methyl ester sample. The sample was dried over anhydrous magnesium sulphate. The solvent (ethyl acetate) was then removed using a rotary evaporator. The unreacted anhydrides were removed at atmospheric pressure using distillation at 80 °C.

The distillation unit can only process about 20 ml of sample each time, limiting the amount of sample that can be processed.

The obtained branched methyl ester sample was then used as precursors for the synthesis of modified triester-derivatives by acetylation with octanoyl chloride to obtain the palm kernel biolubricant (PKBL_E). Fig. 2 shows the reaction scheme for the esterification of EMPKO^o (epoxide).

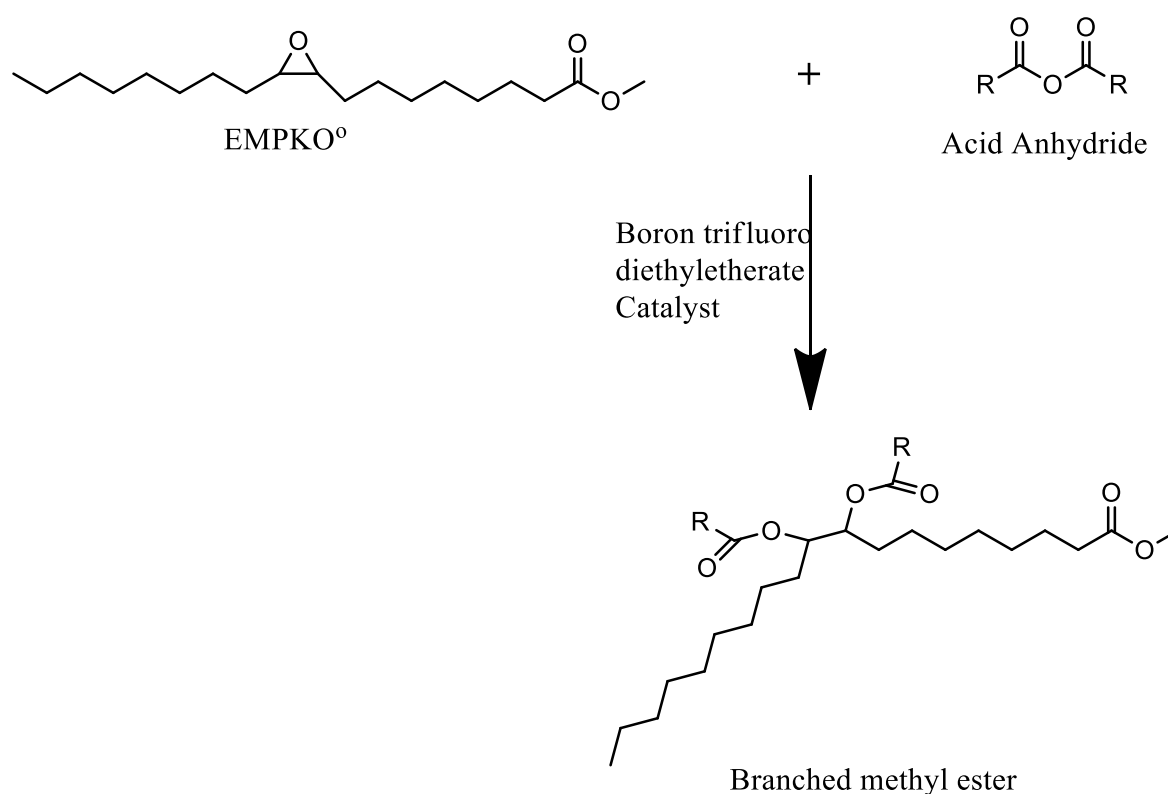


Fig. 2: Reaction Scheme for Esterification of EMPKO^o (epoxide).

3. Results and Discussion

3.1. Transesterification of PKME with TMP for palm kernel biolubricant production

Figs. 3 and 4 show the progress of the transesterification reactions at different times for 3.0 and 4.0 molar-ratios, respectively. From the plots, it could be seen that transesterification advanced stepwise. At first, monoester (ME) formation reached a maximum value. This was immediately followed by diester (DE) formation. At maximum DE formation stage, triester

(TE) formation increased at a fast rate. This was attributed to the fact that during the transesterification of FAME with TMP which occurs stepwise, intermediate products are produced, prior to the final preferred product formation, which is the triester (TE) [25]. Firstly, during the reaction, the ME, that is a single branch polyol ester was formed. However, increasing the ME quantity, would result to immediate conversion to DE with another FAME molecule. Finally, the TE was formed by the reaction of DE and FAME (PKME). It is worth noting from the plots that the TE concentration increased with decrease in concentrations of DE and ME, as evident in the Figs. 3 and 4. This reaction mechanism has been reported by a number of other researchers [4,26-27].

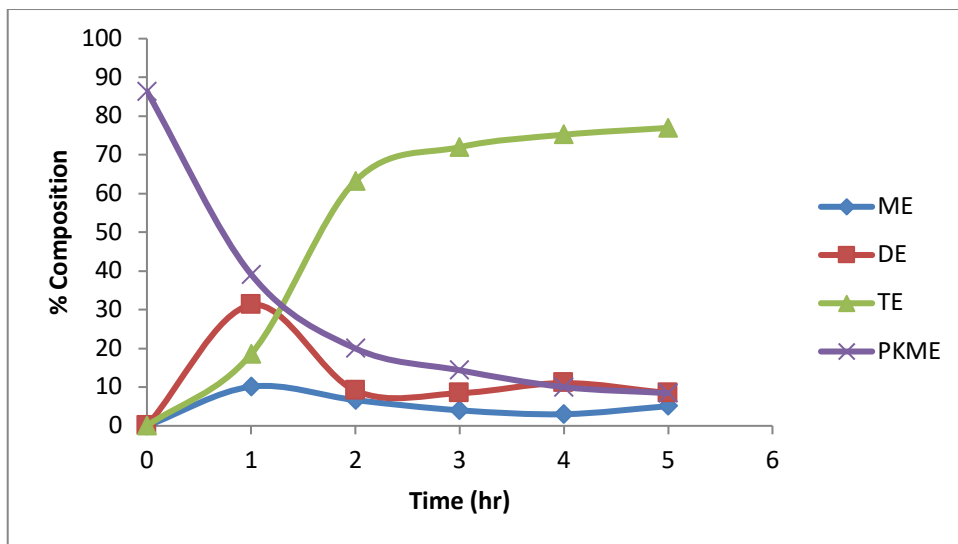


Fig 3: Transesterification between TMP and PKME of 140 °C and 3:1 molar-ratio, using 1 wt % Ca(OH)₂ catalyst

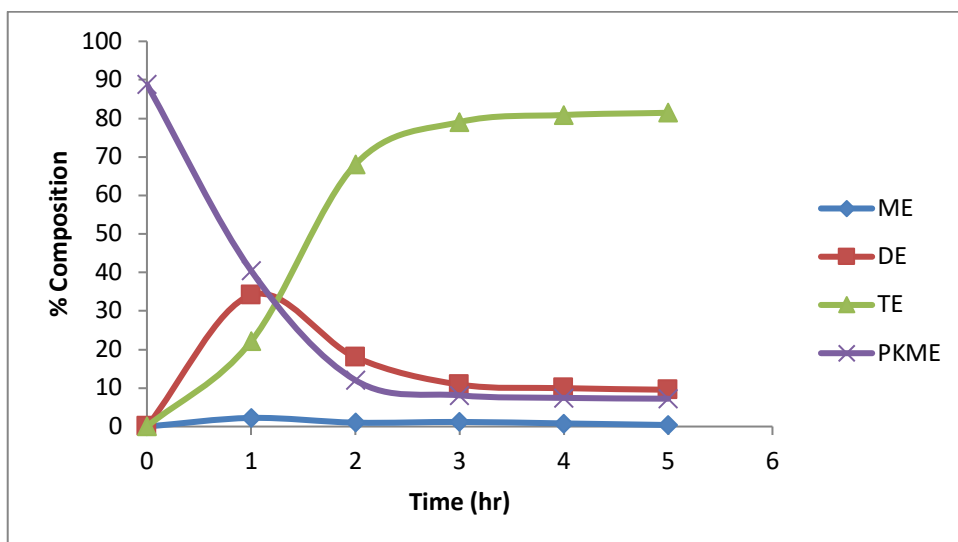


Fig 4: Transesterification between TMP and PKME of 140 °C and 4:1 molar-ratio, using 1 wt % $\text{Ca}(\text{OH})_2$ catalyst.

3.1.1. Temperature Effects

For the determination of temperature effect on synthesis of biolubricant from PKME, experiment was conducted at FAME to TMP molar ratio of 4:1, with catalyst concentration of 1.0% wt/wt of reaction mixture. At these conditions, the reaction was carried out at 80, 100, 120, 140 and 160 °C, in other study the effect of temperature on biolubricant synthesis. Figs. 5 and 6 show the temperature effects results for the synthesis PKO biolubricant. It could be seen from the Fig. 5 that an increase in the temperature, resulted to the increase in TE composition, until at about temperature of 140 °C, when the TE composition increase became negligible. This was attributed to the fact that at higher temperature (see Fig. 6); the quantity of FAME in the reactor was low, due to vaporization, favoring the reverse reaction. In other words, the re-condensation of the FAME vapor back into the reactor. Hence, the reverse reaction would be contained; thereby leading to more esterification of the DE to TE. Therefore, there is need for the condenser water to be cold enough, in other to ensure condensation of the vaporized FAME back into the reactor [4,28].

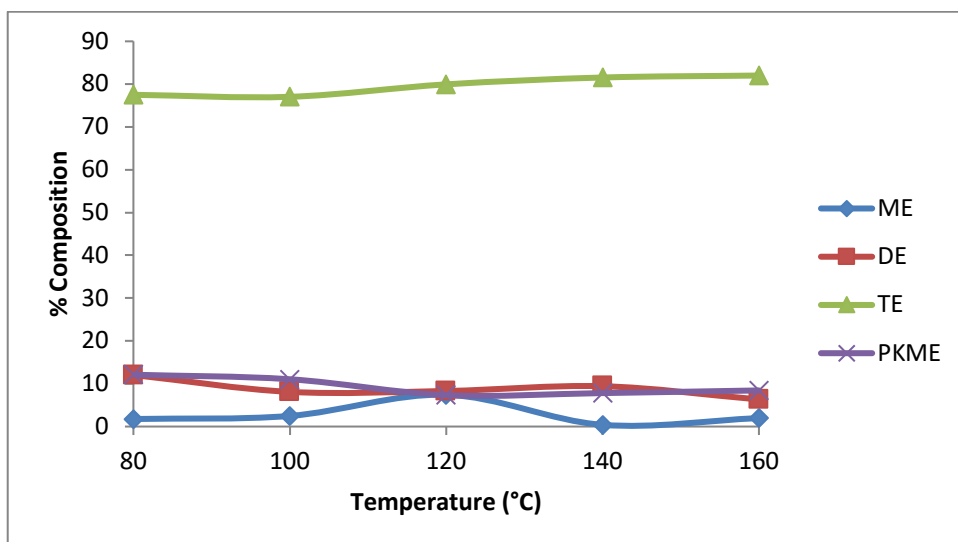


Fig. 5: Effects of temperature on PKME composition at 4:1 PKME-TMP mole ratio and 1% catalyst loading for 5 hrs.

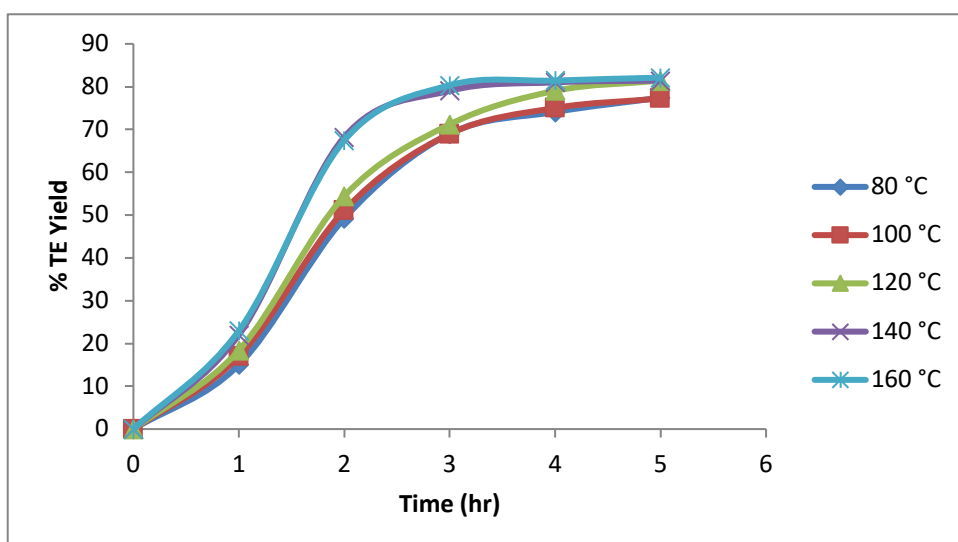


Fig. 6: Temporal yield of PKTE at various temperatures, 4:1 PKME-TMP mole ratio and 1% catalyst loading.

3.1.2. Mole Ratio Effects

In order to ensure improved yield of the triester during the transesterification of FAME with TMP, excess quantity of FAME or TMP is used. This is because transesterification reaction is a reversible reaction. However, in this study, excess FAME was chosen over TMP due to economic reasons of its lower cost. The molar ratio of FAME to TMP was varied at 3:1, 4:1, 5:1, 6:1 and 7:1, at temperature of 100 °C, time of 5hr and $\text{Ca}(\text{OH})_2/\text{wt}$ catalyst weight of 1.0% wt. Fig. 7 shows the effect of PKME: TMP mole ratio on % composition of TMP ester at 100 °C and catalyst loading of 1% each. Then again, Fig. 8 shows the temporal yield of

palm kernel triester (PKTE) at various mole ratios for temperature of 100 °C and 1 % catalyst loading. It could be seen from Fig. 7 that as the molar ratio of FAME: TMP was increased, the yield of TE increased as well. In other to obtain better and more product yield, the reactants molar ratios were kept above the stoichiometric values. This is because the reaction was driven more toward completion. However, in Fig. 8, it was evident that increasing the molar ratio beyond 4:1 gave negligible improvement in TE yield for palm kernel biolubricant. This phenomenon could be attributed to the low rate of conversion of DE to TE, as well as occurrence of reverse reaction that caused the breaking of DE to TE [4,29]. Nouredini and Zhu [29], reported that for the chemical and enzymatic transesterification of rapeseed methyl ester using TMP, maximum conversion was attained at mole ratios of 3.3:1 and 3.5:1, respectively. In this work, it could be seen that the conversion to TE increased from 71.34 to 77.10 % as the mole ratio increased from 3:1 to 4:1 (see Fig. 7). However, a small amount of DE was an added value to the properties of the lubricant. Meanwhile, the large excess of FAME remaining in the final product would affect the physical properties of lube which would require additional energy to remove [26].

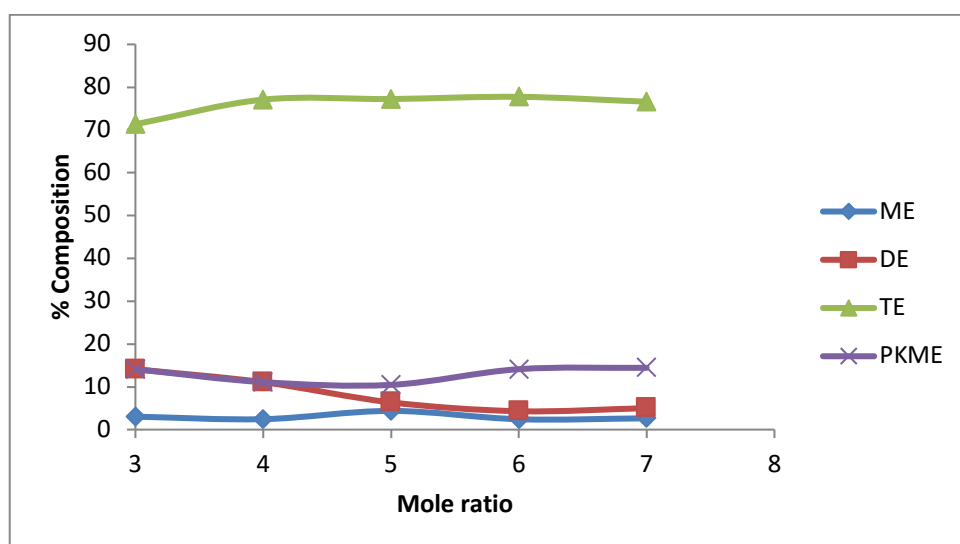


Fig. 7: Effects of PKME: TMP mole ratio on % composition of TMP ester at 100 °C and 1% catalyst loading

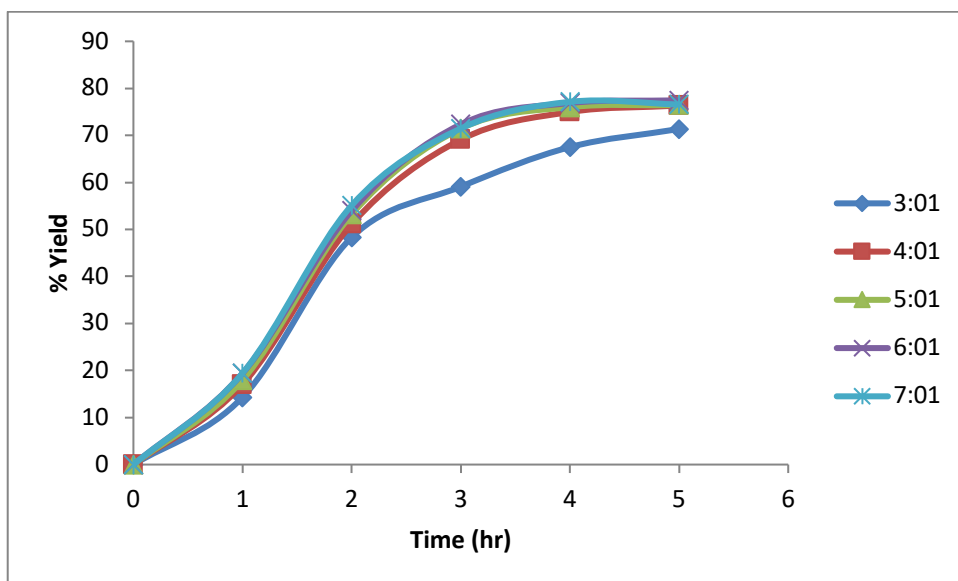


Fig. 8: Temporal yield of PKTE at various mole ratios, 100°C and 1% catalyst loading

3.2. Epoxidation and subsequent esterification of PKME for biolubricant production

The result of the effect of temperature and time at different times and temperatures, on the relative fractional conversion of the palm kernel methyl ester sample to oxirane is presented in Fig. 9. The conditions used for this study were H_2O_2 -ethylenic unsaturation molar ratio of 1.5:1, 2.5 wt% H_2SO_4 catalyst conc., and 1200 rpm stirring speed.

Temperature and time effects on the rate of epoxidation of the palm kernel methyl ester sample, was determined at 35, 45, 55, 65 and 75 °C. The result indicates that the relative fractional conversion to oxirane, increased directly with reaction time during the early stages of the reaction as could be seen in Fig. 9. However, it later started to decrease with additional increase in time of the reaction. This abnormality associated with additional increase in time was due to the commencement of oxirane ring opening [30-31]. Also, it was found that temperature increase favored peracetic acid formation. Hence, the resulting implication was not limited to accelerated epoxidation, but also in enhanced hydrolysis rate; that is oxirane ring opening of the product [32].

Furthermore, Fig. 9 shows the times necessary to achieve maximum relative conversion at different temperatures. As could be seen in the Figure, the time necessary to attain maximum relative conversion were 8, 7.9, 6, 6, and 4 hr., at temperatures of 35, 45, 55, 65 and 75 °C, respectively. From the Fig. 9, it was observed that smaller rates were noticed for the reactions at lower temperatures of 35 and 45 °C. Though, more stable oxirane rings were obtained at these temperatures, compared to those of higher temperatures 55, 65 and 75 °C, which showed higher rate, but more unstable oxirane ring, leading to higher degradation of the epoxide. It is important to state that at the higher temperatures of 55, 65 and 75 °C; the relative conversion of the PKME sample to oxirane attained maximum values in 6, 6 and 4 hr., respectively. Nevertheless, it was noticed that there was decrease in the relative conversion to oxirane with additional increases in time. For instance, at temperature of 75 °C, the observed decrease in the relative conversion to oxirane was very clear since it began after 4 hr. In the same way, at temperatures of 55 and 65 °C, their relative conversion started after 6 hr. Nevertheless, at 35 and 45 °C, more stable rings were obtained for the sample. This is because there was no decrease in the relative conversion to oxirane within the studied time intervals (see Fig 9).

Similar results were also obtained by Agu et al. [2], Goud et al. [32] and Cai et al. [33] for the epoxidations of *Terminalia catappa* L. methyl ester, mahua and soyabean oils, respectively. The highest fractional conversion to oxirane obtained was 0.87, at 75 °C in 4 hr. as shown in Fig 9.

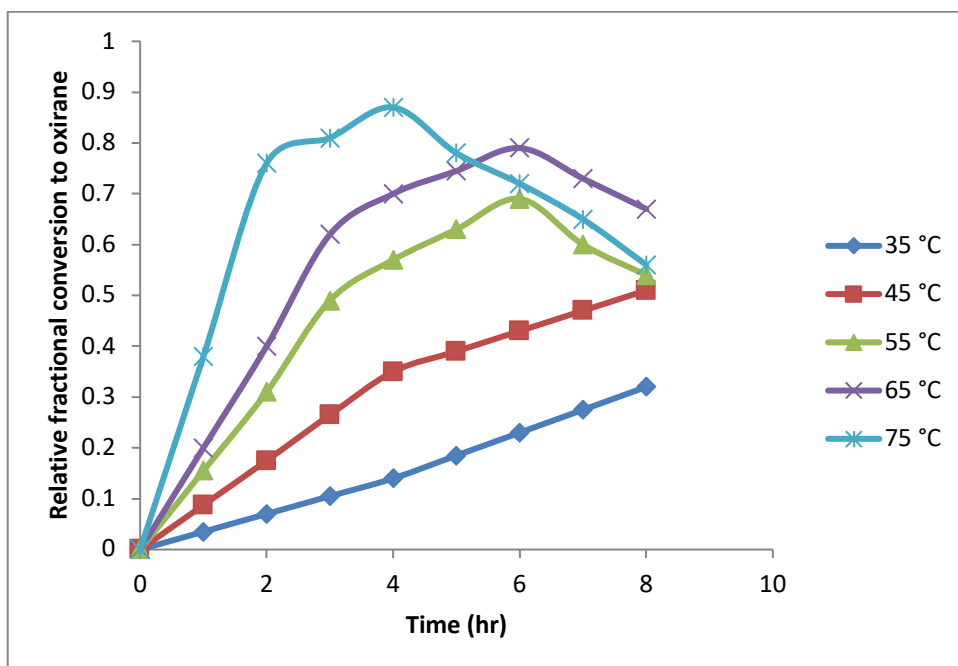


Fig. 9: Effects of temperature and time on relative fractional conversion to oxirane for the epoxidation of palm kernel methyl ester

3.3. Physicochemical properties of PKO and PKO biolubricants

The physicochemical properties of the PKO and the biolubricants produced by transesterification with trimethylolpropane (TMP) and epoxidation-esterification methods are presented in Table 1. The obtained oil yield of palm kernel was 49.82 %. This value was slightly higher than the 47.5 % and 49.2 % yields reported for palm kernel by Ibiam and Anosike [8] and Hossain et al. [34]. However, this value was lower than the 49.9 % yield, reported by Zaidul et al. [35]. This difference in the PKO yields could be attributed to the extraction method used [36].

A number of studies have shown that vegetable oils have short comings with respect to its use as biolubricant without modification of its structure [37-38]. These limitations include thermal, oxidative and hydrolytic instability as well as inadequate low temperature fluidity as a result of their high pour points [1]. These limitations are as a result of the glycerol moiety which is a major constituent in vegetable oil. Most of these problems are significantly reduced by chemical modification of the vegetable oil, in this case PKO. Hence, the reason

for the modification of the PKO using the methods of transesterification with trimethylolpropane (TMP) [1,17] and epoxidation-esterification [37-40].

The synthesis of PKO biolubricant using two stage transesterification methods causes the removal of the β -hydrogen atom from the oil structure. Hence, provides an ester with high oxidative and thermal stability [41]. In this two stage transesterification process, the unstable hydrogen that is bared by the glycerol molecule is substituted by a more stable TMP. At the first stage of the transesterification reaction, the glycerol molecule is removed, while in the second stage, a more effective TMP molecule, replaces the glycerol. Thus, trimethylolpropane triester (TMPTE) that has more superior properties and performance is produced [1].

Similarly, the synthesis of PKO biolubricant was also achieved using the three step synthesis of the methyl ester that involves epoxidation, ring opening and esterification steps. The epoxidation process helps in the removal of unsaturation in the methyl ester by converting them into epoxy-groups that improves the oxidative stability. It is a known fact that the existence of double bonds in vegetable oils chains accelerates oxidative degradation. On the other hand, there are poor low temperature properties in the oil, leading to solidification at lower temperatures like 0 °C. These short comings, limit their application at low operating temperature, especially as biolubricants for automotive and industrial purposes [40]. Hence, suitable method to improve the low temperature flow properties is to attach branching sites at the epoxy carbons. This leads to the need for the ring opening step of this synthesis approach. This was achieved by careful carrying out esterification ring opening reaction using acid anhydride and boron trifluoro diethyletherate catalyst. The obtained branched methyl ester was used as precursors for the synthesis of modified triester-derivatives by acetylation with octanoyl chloride.

Conventional lubricant, the petroleum lubricant sample was analyzed using similar parameters as those determined for the biolubricant. This was to evaluate the properties nearness of the biolubricant samples to the conventional lubricant. Table 1 shows the physicochemical properties of the PKO, palm kernel biolubricat (PKBL_T) synthesized by transesterification of trimethylolpropane (TMP), palm kernel biolubricat (PKBL_E) synthesized by epoxidation-esterification of the methyl ester and the conventional petroleum lubricant.

Generally, it could be seen from the table that the biolubricants samples were more viscous and have higher weight than the petroleum lubricant counterpart. Hence, these properties give rise to the advantages of better mechanical load and thermal resistance of biolubricants over mineral lubricant [1]. Furthermore, the viscosity indices and pour points values of the studied samples were similar to the petroleum lubricant sample. The flash point values of the synthesized biolubricant samples were higher than the PKO sample. This is an indication that the synthesized samples had enhanced thermal resistance as a result of the transesterification with trimethylolpropane (TMP) and epoxidation-esterification reactions. The flash point values of the synthesized biolubricant samples were close to that of petroleum lubricant. Thus, this is an indication of their greater thermal stability.

Table 1: Physicochemical properties of PKO and modified PKO biolubricants

Property	units	PKO	PKBL _T	PKBL _E	Petrolubricant	Methods
Oil yield	%	49.82				AOAC 920.85
Specific gravity	g/ml	0.910	0.990	1.10	0.848	ASTM D1217-15
Viscosity @ 40 °C	cSt	24.08	42.53	44.69	46.476	ASTM D445
Viscosity @ 100 °C	cSt	5.02	10.65	11.42	6.940	ASTM D445
Viscosity index		180	139	132	105	ASTM D2270
Pour point	°C	18	-11	-12	-20	ASTM D97
Flash point	°C	210	235	240	220	ASTM D93

3.3.1. Specific Gravities (SG) of synthesized PKO biolubricants

As could be seen in Table 1, the specific gravity value of PKO biolubricant PKBL_T synthesized by transesterification with trimethylolpropane (TMP) (0.990 g/mL), is similar to that PKBL_E synthesized by epoxidation-esterification (1.10 g/mL). However, it could be seen from the table that there was increase in the specific gravity of these two samples when compared to the SG of the raw PKO 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 PKBL_T and PKBL_E samples, compared to the PKO value, was attributed to increase in molecular complexity resulting from the trimethylolpropane (TMP) backbone and the elongated chain of the triester, resulting from the epoxy ring opening, respectively [1,40]. It could be seen that the specific gravity value for the biolubricant samples were higher than the petrolubricant. This could be attributed to chemical structural change in the constituent molecules. It is worth noting that the specific gravity change leads 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 [42]. 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 [42]. 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 [1,42].

3.3.2. Viscosities of the synthesized PKO biolubricants samples at 40 °C and at 100 °C

The viscosities of PKO biolubricants synthesized by transesterification with TMP PKBL_T were 42.53 cSt at 40 °C and 10.65 cSt at 100 °C, respectively. Similarly, the viscosities of PKO biolubricants synthesized by epoxidation-esterification PKBL_E were 44.69 cSt at 40 °C

and 11.42 cSt at 100 °C, respectively. From the values in Table 1, it could be seen that viscosities values of the PKBL_E sample were comparatively higher than those of the PKBL_T sample. For the PKO sample, its viscosity was lower than the values reported for PKO and palm oil, by Alang et al. [1] and Reddy et al. [43], respectively. However, the PKO sample viscosity was lower than the value reported for Jatropha oil by Menkiti et al. [4]. These values for PKO biolubricant samples were less than those of biolubricant from PKO reported as 480.63 cSt at 40 °C and 20.54 cSt at 100 °C, by Alang et al. [1]. Also, the values of the viscosities of PKO biolubricants in this work were lower, when compared to Jatropha biolubricants with values of 55.17 cSt at 40 °C and 10.96 cSt at 100 °C, as reported by Bilal et al. [44]. The values for PKO biolubricant are comparable with those of petroleum lubricants which were evaluated to be 46.476 cSt and 6.940 cSt, at 40 °C and 100 °C, respectively. However, it is vital to state that the viscosities at 100 °C of the PKO bio-lubricants samples obtained in this work were greater than that of the petroleum lubricants. As such, the synthesized PKO biolubricants exhibits greater thermal stability and can endure greater mechanical stress than petroleum lubricants.

3.3.3. Viscosity Index

The viscosity index values for the PKO biolubricant synthesized by transesterification with trimethylolpropane (TMP) PKBL_T, synthesized by epoxidation-esterification PKBL_E, and petroleum lubricant are 139, 132 and 105, respectively. These values are 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 PKO in this work is 180. This value is slightly lower than 185,

reported by Alang et al. [1] for PKO. Also, this value was lower than the 233 viscosity index value for Jatropha oil, reported by Menkiti et al. [4].

3.3.4. Pour Points

The temperature, at which oil solidifies enough to resist flow, is the pour point of the oil sample [42]. The pour point reduced from 18 °C for PKO to – 11 °C and – 12 °C for biolubricants after double transesterification and epoxidation-esterification processes, respectively. However, the pour point of the petroleum lubricant is – 20 °C. Hence, these results show that the pour point of the biolubricants and petro-lubricant are good enough for to permit their use at low temperatures. This was possible because, in the biolubricants, the products thermal resistance was greatly enhanced, due to the fact that the thermally fragile glycerol in the PKO triglycerides are 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 PKO biolubricants, compared to the PKO. Similar results were obtained by Alang et al. [1] and Musa [42] for the synthesis of biolubricant using PKO; as well as by Bello et al. [45], for the synthesis of biodiesel from PKO.

3.3.5. Flash Points

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 [2]. The flash points of PKO and palm kernel biolubricants samples PKBL_T and PKBL_E were 210 °C, 235 °C and 240 °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 vapor is emitted from the lubricant to temporarily ignite a flame [1]. 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 Alang et al. [1] (>210) and Salih et al. [17] (>300), for PKO biolubricant. These flash point values of the obtained PKO biolubricants samples were also in the range of those reported by Aji et al. [38] for Neem biolubricant (262 °C) and by Bilal et al. [44] for Jatropha biolubricant (274 °C).

3.4. Fourier Transform Infrared (FTIR) analyses of PKO and PKO biolubricants

The surface chemistry of the extracted PKO sample and the synthesized biolubricants samples were analyzed using FTIR spectroscopy in order to determine the functional groups present in them. The results in Figs. 10 – 12 were analyzed and likened with known signature of identified materials in the FTIR library [46]. For all the samples, the main peaks of importance would be highlighted and briefly discussed.

For the PKO sample (Fig. 10), 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 2020.284 cm⁻¹ is characteristics of combination N – H stretching, combination O – H stretching, indicating the presence of organic compounds. Furthermore, the peaks centered 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. 11 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 [47]. 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. 12 indicates the FTIR spectrum ranges of the PKO biolubricant obtained by the epoxidation-esterification of the methyl ester sample. This spectrum indicates that epoxidation had taken place. For instance, the appearance of the band peaks of 1100 cm^{-1} and $1110 - 1290\text{ cm}^{-1}$, which were not present in the methyl ester sample, is characteristics of the epoxide. This is because the functional groups of C – O – C stretching of ethers oxirane ring and Aliphatic C – O stretching of esters, indicate the presence of oxygen-containing compounds [46]. The band corresponding to the carboxylic acid functional group is located at $3509 - 3533\text{ cm}^{-1}$. The presence of this group is associated with the ester hydrolysis during epoxidation reaction [22]. Furthermore, the band corresponding to the alkane group is located at $2850 - 2873\text{ cm}^{-1}$. The presence of this functional group which was not present in the raw PKO sample indicates the stability of the biolubricant sample obtained by epoxidation-esterification. Finally, predominance of epoxy groups $1100 - 1290\text{ cm}^{-1}$, indicates that epoxidation reaction actually occurred.

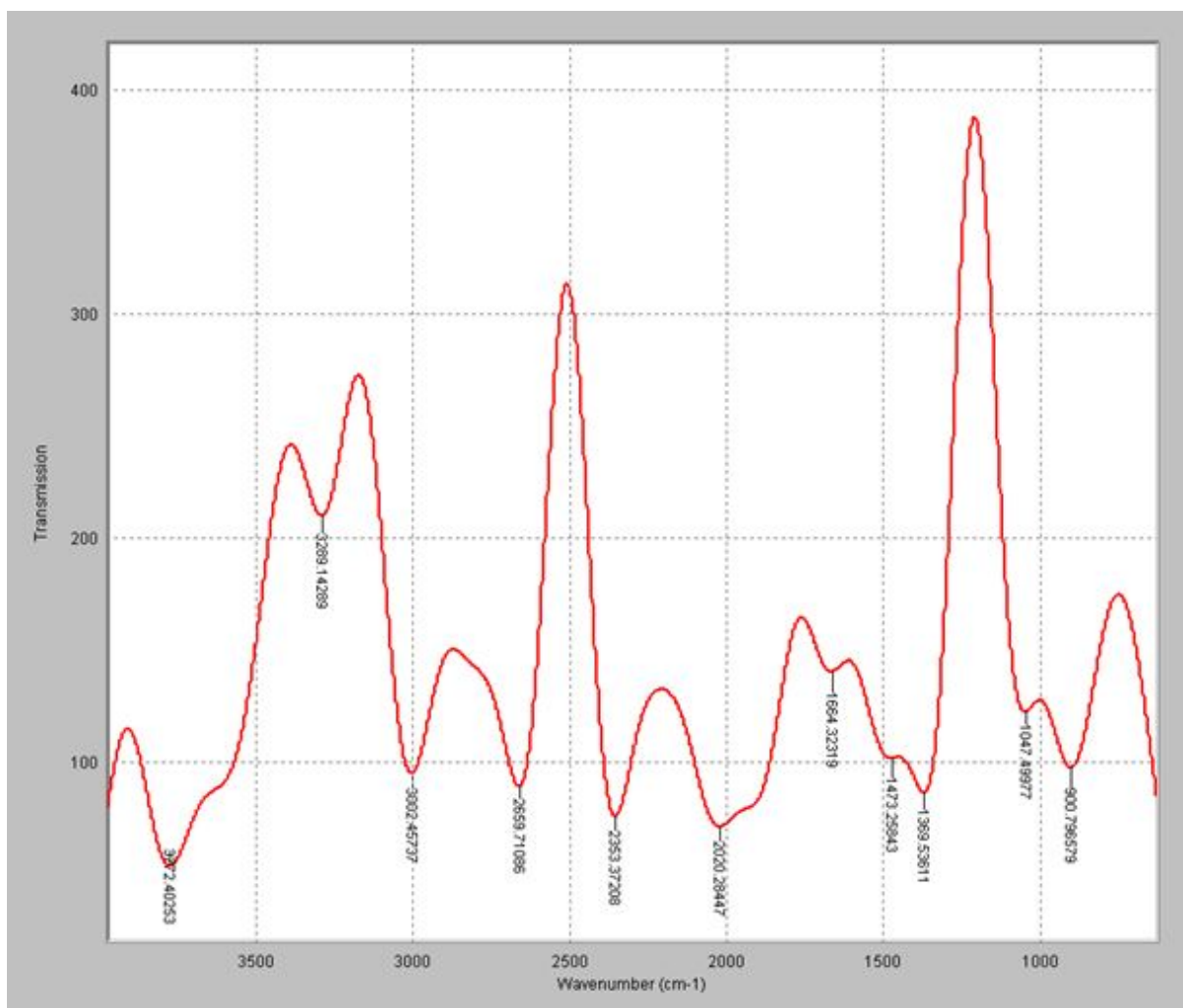


Fig. 10: FTIR spectrum of PKO

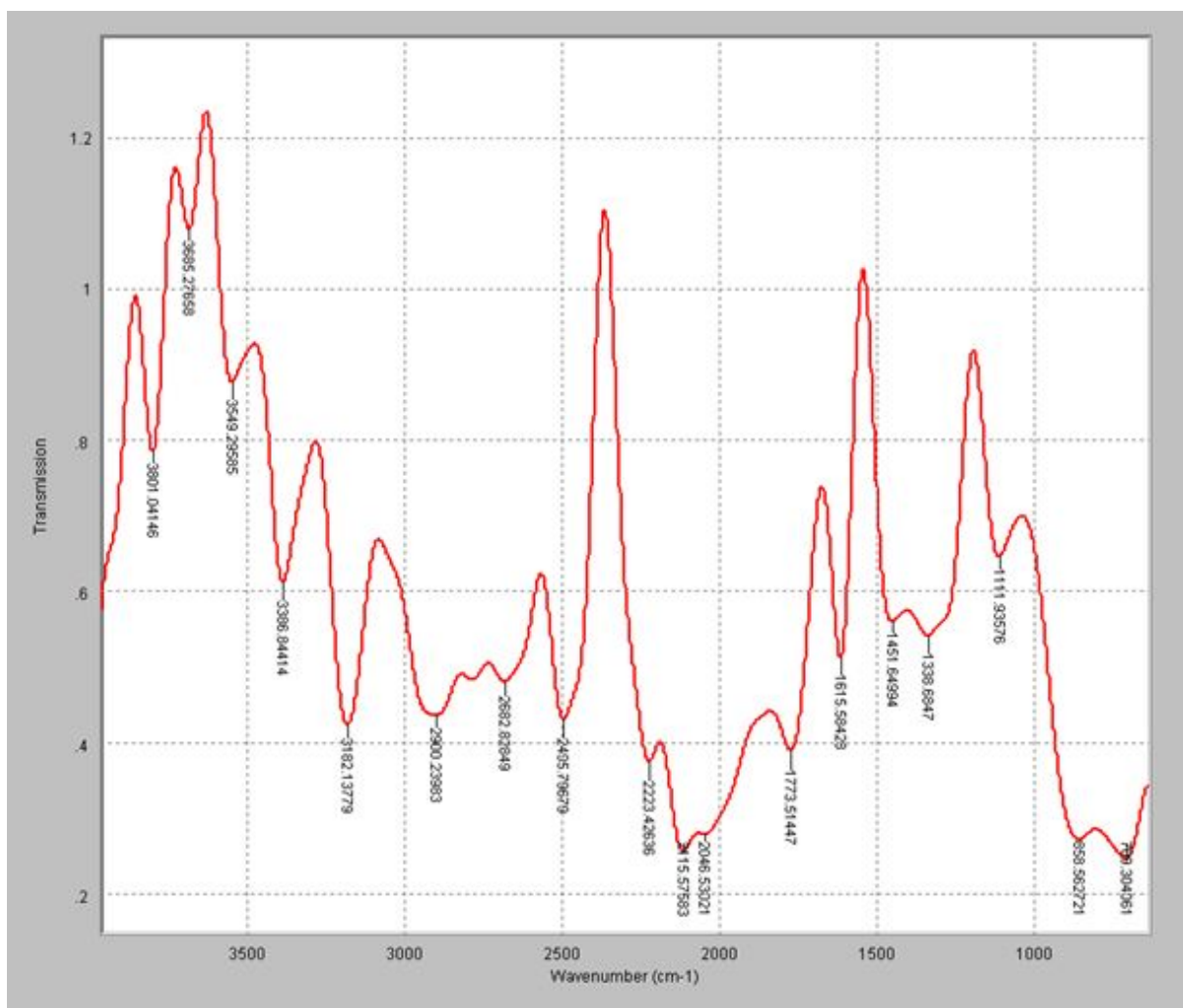


Fig. 11: FTIR spectrum of PKO biolubricant obtained by transesterification of methyl esters and TMP

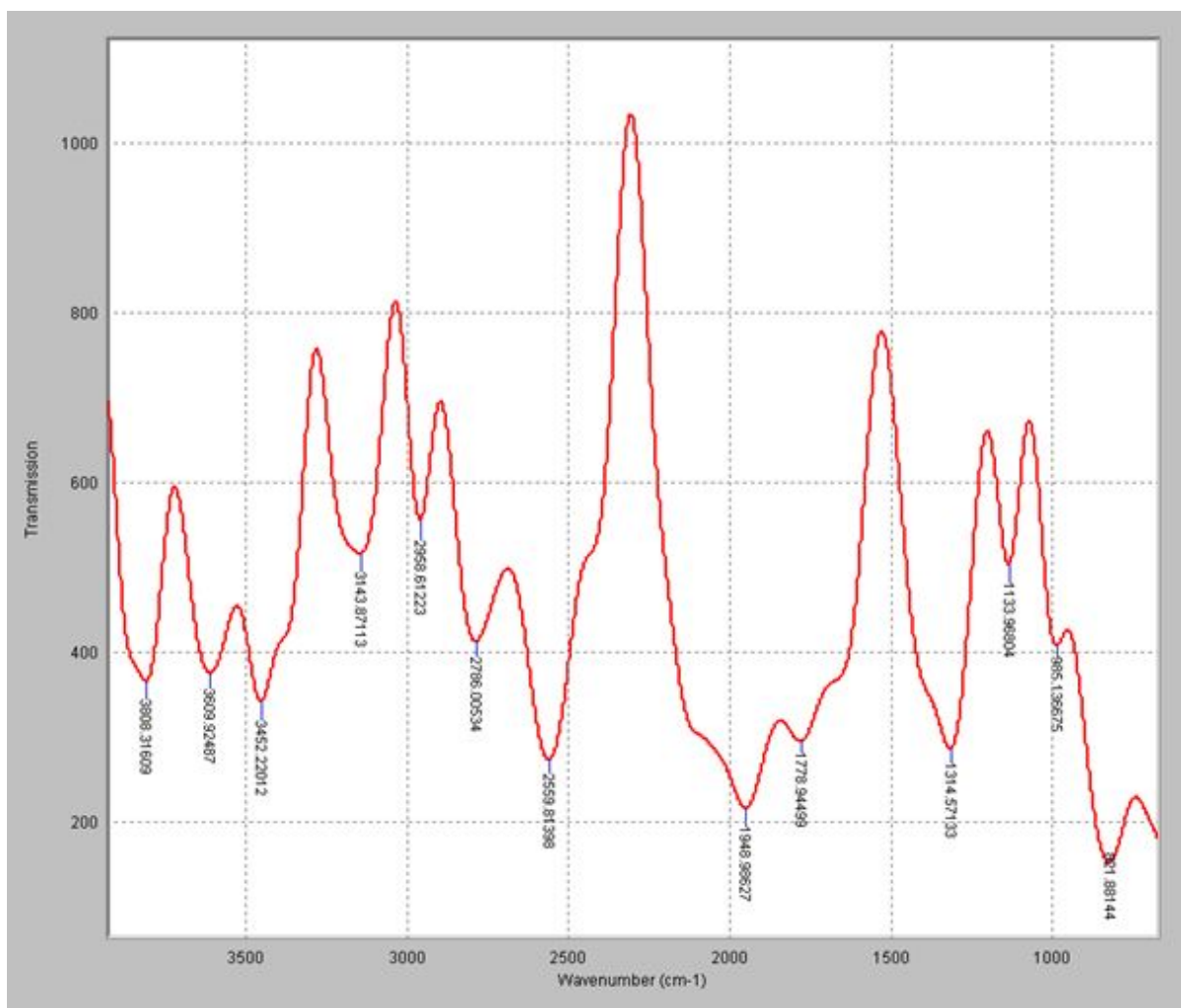


Fig. 12: FTIR spectrum of PKO biolubricant obtained by epoxidation-esterification of methyl ester sample

3.5. Fatty Acid composition of PKO, and synthesized biolubricant

The fatty acid compositions of palm kernel oil (PKO), PKO biolubricant synthesized by transesterification with trimethylolpropane (TMP) (PKBL_T), and PKO biolubricant synthesized by epoxidation-esterification (PKBL_E) methods are presented in Table 2. Similarly, the fatty acid profile of PKO, PKBL_T, and PKBL_E are presented in Figs. 13, 14 and 15, respectively. From the results in the table, it could be seen that the saturated and unsaturated fatty acid compositions of PKO, PKBL_T and PKBL_E, were (72.69 % and 27.31 %), (81.81 % and 18.19 %), and (83.45 % and 16.55 %), respectively. This is an indication that the PKO, PKBL_T and PKBL_E samples were all highly saturated. For the PKO 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 PKO by Alamu et al. [48]. However, there is the need to further improve on the saturated level of the PKO using modification prior to their possible application as biolubricant [4].

Table 2: Fatty acid compositions of the PKO, PKBL^T and PKBL^E samples

Fatty acid	Fatty acid Type	PKO (%)	PKBL ^T (%)	PKBL ^E (%)
C 8:0 (Caprylic acid)	Saturated	0.11	0.58	1.89
C10:0 (Capric acid)	Saturated	5.08	2.13	6.71
C12:0 (Lauric acid)	Saturated	41.85	47.61	45.36
C14:0 (Myristic acid)	Saturated	18.34	20.42	19.08
C16:0 (Palmitic acid)	Saturated	6.13	8.52	7.56
C18:0 (Stearic acid)	Saturated	1.18	2.55	2.85
C18:1 (Oleic acid)	Unsaturated	17.45	16.11	15.44
C18:2 (Linoleic acid)	Unsaturated	9.86	2.08	1.11
Saturated fatty acids (%)		72.69	81.81	83.45
Unsaturated fatty acid (%)		27.31	18.19	16.55
Total (%)		100.00	100.00	100.00

From the results presented in Table 2, it could be observed that the saturated and unsaturated fatty acid compositions of PKBL_T, were 81.81 % and 18.19 %, respectively. These results show that, the percentage compositions of the saturated fatty acids for the PKBL_T sample increased, while that of the unsaturated decreased, after transesterification of the PKO sample using TMP. This could be due to the heat assimilation. This is because as the heating temperature rises, it results to in the fatty acids modification. Hence, the saturation level increases due to decreased prevalence of two or three double bonds [49]. Henceforth, this results in the polyunsaturated fatty acids (PUFA) decrease, with corresponding increase in the saturated fatty acids (SFA) [50]. Therefore, transesterification of PKO using TMP increases its saturation level, making the modified oil more usable as biolubricant. The predominant saturated fatty acid in PKBL_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 *Jatropha curcas* oil [4].

From the results presented in Table 2, it could be seen that the saturated and unsaturated fatty acid compositions of PKBL_E sample, were 83.45 % and 16.55 %, respectively. From these results (Table 2), it could be seen that even though the percentage compositions of the saturated fatty acids increased, leading to decrease in percentage of unsaturated fatty acid (oleic acid and linoleic acid). It could be observed that there was more increase in the percentage of saturated fatty acids present in the PKBL_E sample, when compared to that of PKBL_T samples. 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 bond [49]. These explanations, substantiates the reason for the decrease and increase of the unsaturated fatty acids (UFA) and saturated fatty acids (SFA), respectively [50]. The improvements in the stability of the PKBL_E and PKBL_T samples were due to increase in SFA samples as evident in the Table 2. Like in the PKO and PKBL_T, the predominant saturated and unsaturated fatty acids in PKBL_E sample, were lauric acid and oleic acid, respectively.

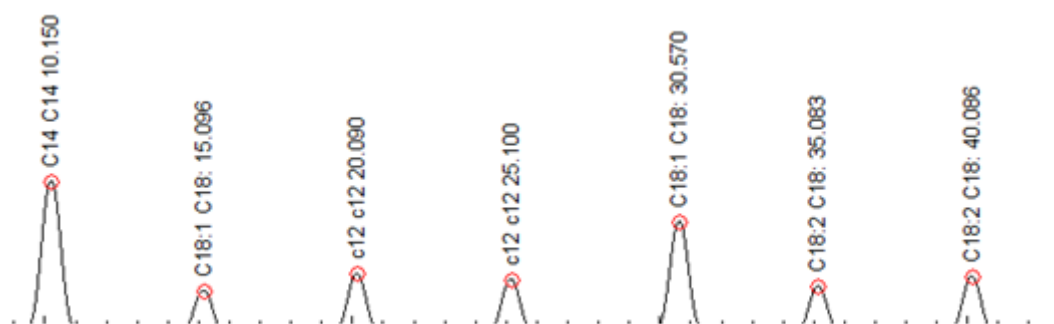


Fig. 13: Fatty acid profile of PKO

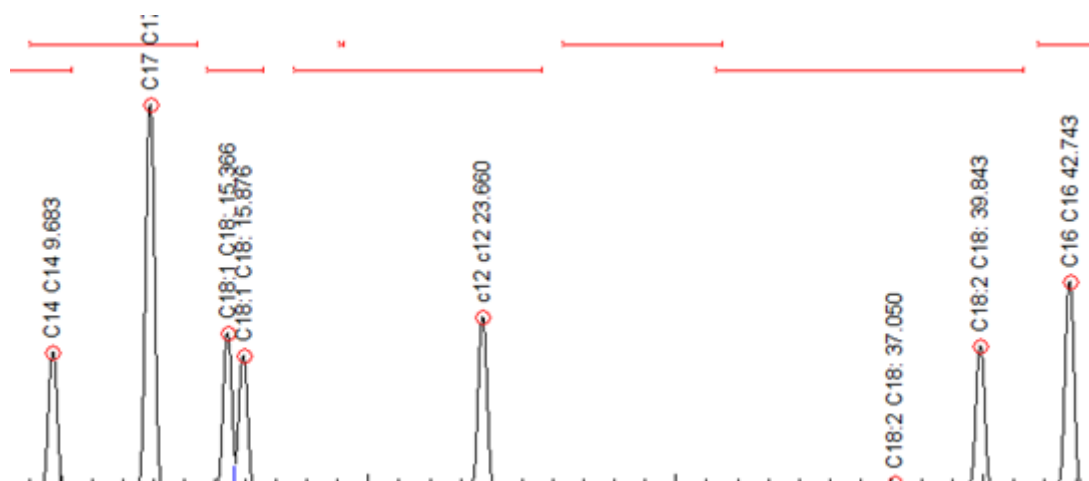


Fig. 14: Fatty acid profile of PKBL_T

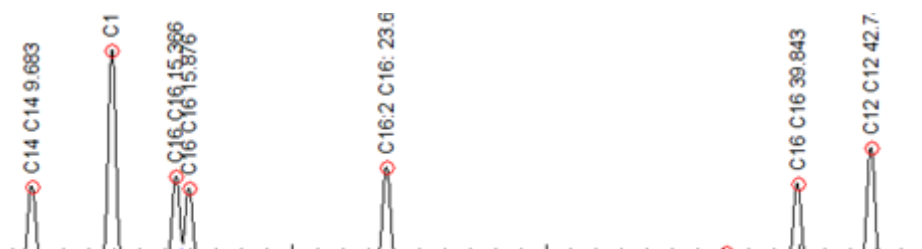


Fig. 15: Fatty acid profile of PKBL_E

4. Conclusion

The production of biolubricant from PKO using transesterification PKME using TMP and epoxidation-esterification processes was achieved successfully. However, the PKBL_E sample, produced by transesterification of PKBL_T using TMP, showed conformed better to the stipulated standard, when compared to the PKBL_E sample obtained by the epoxidation-esterification method. That notwithstanding, both samples have shown potential for utilization as ecofriendly bio-lubricant. The presence of the C – H, OH functional groups identified by the FTIR results, is an indication that they would enhance the biodegradability of the produced bio-lubricants samples. The effects of time, temperature and mole ratio significantly affected the transesterification reaction with TMP; while time, temperature and molar ratio of H₂O₂ significantly influenced the epoxidation reaction. Therefore, chemical

620 modifications of PKO for bio-lubricant production using the aforementioned methods were
621 useful in successful development of ecofriendly PKO bio-lubricant samples.

622 **Acknowledgement**

623 The authors wish to acknowledgement the management of Spring Board Laboratory, Awka,
624 Nigeria where the analyses were done.

625 **Conflict of Interest statement**

626 Authors have no conflict of interest relevant to this article.

627 **Nomenclature**

628	AOAC	Association of Official Analytical Chemists'
629	DE	Diester
630	EMPKO ^o	Epoxy Methyl Ester (Oxirane) of Palm Kernel Oil
631	FAME	Fatty Acid Methyl Ester
632	FTIR	Fourier Transform Infrared
633	GC	Gas Chromatography
634	ME	Monoester
635	PAA	Peracetic Acid
636	PKBL _E	Palm Kernel Biolubricant obtained by Epoxidation-Esterification
637	PKBL _T	Palm Kernel Biolubricant obtained by transesterification of TMP
638	PKME	Palm Kernel Methyl Ester
639	PKO	Palm Kernel Oil
640	PKTE	Palm Kernel Triester
641	PUFA	Polyunsaturated Fatty Acids
642	RPM	Revolutions per Minute
643	SFA	Saturated Fatty Acids

644	TE	Triester
645	TMP	Trimethylolpropane
646	TMPTE	Trimethylolpropane Triester
647	UFA	Unsaturated Fatty Acids

648 **References**

- 649 [1] M.B. Alang, M.K. Ndikontar, Y.M. Sani, P.T. Ndifon, Synthesis and Characterisation of a
650 Biolubricant from Cameroon Palm Kernel Seed Oil Using a Locally Produced Base
651 Catalyst from Plantain Peelings. *Green and Sustainable Chemistry*, 8 (2018), 275 – 287.
- 652 [2] C.M. Agu, M.C. Menkiti, J.T. Nwabanne, O.D. Onukwuli, Comparative assessment of
653 chemically modified *Terminalia catappa* L. kernel oil samples – A promising ecofriendly
654 transformer fluid. *Industrial Crops and Products*, 140 (2019), 111727.
655 <https://doi.org/10.1016/j.indcrop.2019.111727>.
- 656 [3] A.U. Ofoefule, C. Esonye, O.D. Onukwuli, E. Nwaeze, C.S. Ume, Modeling and
657 optimization of African pear seed oil esterification and transesterification using artificial
658 neural network and response surface methodology comparative analysis. *Industrial Crops
659 and Products*, 140 (2019), 111707.
- 660 [4] M.C. Menkiti, O. Ocheje, C.M. Agu, Production of environmentally adapted lubricant
661 basestock from *Jatropha curcase* specie seed oil. *International Journal of Industrial
662 Chemistry* (2017), DOI 10.1007/s40090-017-0116-1
- 663 [5] R. Yunus, A. Fakhru'l-Razi, T. Ooi, S. Iyuke, J. Perez, Lubrication properties of
664 trimethylolpropane esters based on palm oil and palm kernel oils. *Eur J Lipid Sci Technol*
665 60 (2004), 52–60.
- 666 [6] M. Menkiti, H. Anaehobi, K. Oyoh, P. Nnaji, Process Optimization and Kinetics of
667 Biolubricant Synthesis from Fluted Pumpkin Seed. *European Scientific Journal*, 1(27)
668 (2015), 1857 – 7881.

- [7] J.A.C. da Silva, V.F. Soares, R. Fernandez- Lafuente, A.C. Habert, D.M.G. Freire, Enzymatic production and characterization of potential biolubricants from castor bean biodiesel. *Journal of Molecular Catalysis B: Enzymatic*. 122 (2015), 323–329.
- [8] J.A. Ibiam, P.O. Anosike, Extraction and Characterization of Palm Kernel oil from the Kernel of Palm Tress (*Elaeis Guineensis*). *International Journal of Current Research*, 6(5) (2014), 6696 – 6698.
- [9] C.G. Okeke, S.I. Oluka, Review of Palm Kernel oil Processing and Storage Techniques in South East Nigeria. *Journal of Experimental Research*, 5(1) (2017), 50 – 56.
- [10] T.S. Tang, P.K. Teoh, Palm Kernel Oil Extraction-The Malaysian Experience. *Journal of American Oil Chemists' Society*, 62(2) (1985), 254 – 258.
- [11] R. Sarku, Palm Kernel Processing for income and employment in Kwaebibirem District, Ghana. *Asian Journal of Agricultural Extension, Economics and Sociology*, 16(2) (2017), 1 – 14.
- [12] S.O. Kareem, E.I. Falokun, S.A. Balogun, O.A. Akinloye, S.O. Omeike, Enzymatic biodiesel production from palm oil and palm kernel oil using free lipase. *Egyptian Journal of Petroleum* (2016) <http://dx.doi.org/10.1016/j.ejpe.2016.09.002>.
- [13] E.K. Heikal, M.S. Elmelawy, S.A. Khalil, N.M. Elbasuny, Manufacturing of environment friendly biolubricants from vegetable oils. *Egyptian Journal of Petroleum*, (2016) <http://dx.doi.org/10.1016/j.ejpe.2016.03.003>.
- [14] R. Yunus, A. Fakhrul-Razi, T.L. Ooi, D.R.A. Biak, S.E. Iyuke, Kinetics of Transesterification of Palm-Based Ester with Trimethylolpropane. *Journal of American Oil Chemists' Society*, 81(5) (2004), 497 – 503.
- [15] A.S. Shote, E. Betiku, A.A. Asere, Characteristics of CO and NO_x emissions from combustion of transmethylated palm kernel oil-based biodiesel blends in a compression ignition engine. *Journal of King Saud University – Engineering Sciences* (2018).

<https://doi.org/10.1016/j.jksues.2018.02.005>.

- [16] A.A. Abdelmalik, A.P. Abbott, J.C. Fothergill, S. Dodd, R.C. Harris, Synthesis of a base stock for electrical insulating fluid based on palm kernel oil. *Industrial Crops and Products*, 33 (2011) 532 – 536.
- [17] N. Salih, J. Salimon, F.N. Jantan, Synthesis and Characterization of Palm Kernel Oil Based Trimethylolpropane Ester. *Asia Journal of Chemistry*, 25(17) (2013), 9751 – 9754.
- [18] AOAC., Official methods of Analysis, fifteenth ed. Association of Official Analytical Chemists, Washington, D.C, 1990.
- [19] G. Zahedi, A. Azarpour, Optimization of supercritical carbon dioxide extraction of passiflora seed oil. *Journal of Supercritical Fluids*, 58 (2011), 40 – 48.
- [20] K. Surapoj, B. Suchada, N. Chawalit, Effects of transesterification conditions on synthesis of trimethylolpropane esters. In: *Pure and applied chemistry international conference (2013) (PACCON 2013)*.
- [21] R. Yunus, A. Fakhrulrazi, T.L. Ooi, S.E. Iyuke, A. Idris, Preparation and characterization of trimethylolpropane esters from palm kernel oil methyl esters. *J Oil Palm Res* 15(2) (2003), 42–49.
- [22] S. Arumugam, G. Sriram, T. Rajmohan, Multi-Response Optimization of Epoxidation process parameters of rapeseed oil using response surface methodology (RSM)-Based Desirability Analysis. *Arabian Journal of Science and Engineering*, 39 (2014), 227 – 2287.
- [23] S. Arumugam, G. Sriram, Synthesis and characterisation of rapeseed oil bio-lubricant its effect on wear and frictional behaviour of piston ring–cylinder liner combination. *Journal of Engineering Tribology*, 227(1) (2012), 3 – 15.
- [24] B.K. Sharma, Z. Liu, A. Adhvaryu, S.Z. Erhan, One-Pot Synthesis of Chemically

Modified Vegetable Oils. *Journal of Agriculture Food Chemistry*, 56 (2008), 3049 – 3056.

[25] A. Campanella, E. Rustoy, A. Baldessari, M.A. Baltanas, Lubricants from chemically modified vegetable oils. *Bioresource Technology* 101 (2010), 245–254.

[26] M.C. Menkiti, O. Ocheje, K.B. Oyoh, O.D. Onukwuli, Synthesis and tribological evaluation of sesame oil-based trimethylolpropane ester, *Journal of the Chinese Advanced Materials Society*, 3(2) (2015), 71 – 88.

[27] P.K. Sripada, Comparative Tribological Property Evaluation of Trimethylolpropane based Biolubricants derived from Methyl Oleate and Canola. *Biodiesel*, (2012), 56-57.

[28] P. Nagendramma, S. Kaul, Development of Ecofriendly /biodegradable lubricants: An overview”, *Renew. Sustain. Ener. Rev.*, 16 (2012) 764 – 774.

[29] H. Nouredдини, D. Zhu, Kinetic of Transesterification of Soybean Oil. *Journal of American Oil Chemists’ Society*, 74 (11) (1997), 1457 – 1463.

[30] E.U. Ikhuoria, R.O. Obuleke, F.E. Okieimen, Studies on the epoxidation of the Methyl Esters of *Parkia Biglobosa* Seed Oil. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 44 (2007), 235 – 238.

[31] C. Shuangfei, W. Lisheng, Epoxidation of Unsaturated Fatty Acid Methyl Esters in the Presence of SO₃H-functional Bronsted Acidic Ionic Liquid as Catalyst. *Chinese Journal of Chemical Engineering*, 19(1) (2011), 57 – 63.

[32] V.V. Goud, A.V. Patwardhan, N.C. Pradhan, Studies on the epoxidation of mahua oil (*Madhumica indica*) by hydrogen peroxide. *Bioresource Technology*, 97 (2006), 1365 – 1371.

[33] C. Cai, H. Dai, R. Chen, C. Su, X. Xu, S. Zhang, L. Yang, Studies on the kinetics of in situ epoxidation of vegetable oils. *European Journal of Lipid Science and Technology*, 110 (2008), 341 – 346.

- [34] M.S. Hossain, N.N. Norulaini, A.A. Naim, A.M. Zulkhairi, M. Bennama, A.M. Omar, Utilization of the supercritical carbon dioxide extraction technology for the production of deoiled palm kernel cake. *Journal of CO₂ Utilization*, 16 (2016), 121-129.
- [35] I.S.M. Zaidul, N.N. Norulaini, A.M. Omar, Y. Sato, R.L. Smith Jr, Separation of palm kernel oil from palm kernel with supercritical carbon dioxide using pressure swing technique. *Journal of Food Engineering* 81(2) (2007), 419-428.
- [36] W. Almeida da Costa, C.E. Pereira de Lima, F.W.F. Bezerra, M. Santana de Oliveira, P. d-N. Bezerra, F.C.S. Pires, A.P. Silva, J. Neves da Cruz, S.G. Silva, P.A. Sarges, R. Nunes de Carvalho Junior, *African Journal of Biotechnology*, 18(5) (2019), 101-111.
- [37] R. Yunus, *Biobased Lubricants; Harnessing the Richness of Agriculture Re-sources*. University Putra Malaysia Press, (2015), 15-50. <http://www.penerbit.upm.edu.my>.
- [38] M.M. Aji, S.A. Kyari, G. Zoaka, Comparative Studies between Bio Lubricants from Jatropha Oil, Neem Oil and Mineral Lubricant (Engen Super 20w/50). *Applied Research Journal*, 1 (2015), 252 – 257.
- [39] J. Salimon, N. Salih, E. Yousif, Biolubricants: Raw materials, chemical modifications and environmental benefits. *European Journal of Lipids Science and Technology*, 112 (2010), 519 – 530.
- [40] J. Salimon, N. Salih, E. Yousif, Improvement of pour point and oxidative stability of Synthetic ester basestocks for biolubricant applications. *Arabian Journal of Chemistry*, 5 (2012), 193 – 200.
- [41] H. Wagner, R. Luther, T. Mang, *Lubricant Base Fluids Based on Re-newable Raw Materials: Their Catalytic Manufacture and Modification*. *Applied Catalysis A*, (2001), 221, 429. [https://doi.org/10.1016/S0926-860X\(01\)00891-2](https://doi.org/10.1016/S0926-860X(01)00891-2).
- [42] J.J. Musa, Evaluation of the Lubricating Properties of Palm Kernel Oil. *Leonardo Electronic Journal of Practices and Technologies*, 14 (2009), 107-114.

- [43] K.S.V.K. Reddy, N. Kabra, U. Kunchum, T. Vijayakumar, Experimental Investigation on Usage of Palm Oil as a Lubricant to Substitute Mineral Oil in CI Engines. Chinese Journal of Engineering (2014), <http://dx.doi.org/10.1155/2014/643521>.
- [44] S.I. Bilal, I. Mohammed-Dabo, M. Nuhu, S. Kasim, I. Almustapha, Y.A. Yamusa, Production of Biolubricant from *Jatropha curcas* Seed Oil. Journal of Chemical Engineering and Material Science, 4 (2013), 72 – 79.
- [45] E.I. Bello, B. Oguntuase, A. Osasona, T.I. Mohammed, Characterization and engine testing of palm kernel oil biodiesel. European Journal of Engineering and Technology, 3(3) (2015), 2056-5860.
- [46] S. Barbara, Analytical Techniques in Science. Infrared Spectroscopy; Fundamentals and Application: Wiley, 2004.
- [47] D.W. Mayo, F.A. Miller, R.W. Hannah, Spectra of Carbonyl Compounds of All Kinds (Factors Affecting Carbonyl Group Frequencies); Course Notes on the Interpretation of Infrared and Raman Spectra. Chapter 7, John Wiley & Sons, Inc., Hoboken, (2003) 179 – 204.
- [48] O.J. Alamu, T.A. Akintola, C.C. Enweremadu, A.E. Adeleke, Characterization of palm-kernel oil biodiesel production through NaOH-catalyzed transesterification process. Scientific Research and Essay, 3(7) (2008), 308 – 311.
- [49] M.E. Guerzoni, R. Lanciotti, P.S. Cocconcelli, Alteration in cellular fatty acid composition as a response to salt, acid, oxidative and thermal stresses in *Lactobacillus helveticus*. Microbiology, 147 (2001), 2255 – 2264.
- [50] A.M. Sharoba, M.F. Ramadan, Impact of Frying on Fatty Acid Profile and Rheological Behaviour of Some Vegetable Oils. Journal of Food Process Technology (2012), <http://dx.doi.org/10.4172/2157-7110.1000161>.