



Synthesis and Optimization Process of Ethylene Glycol-Based Bio-lubricant from Palm Kernel Oil (PKO)

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ABSTRACT

Internationally exploited lubricants are derived from coal and petroleum. Due to their high consumption and effects of their long-term pollution on the environment, it is imperative to use renewable and cheap feedstock for the synthesis of bio-based lubricants. This study presents the synthesis and optimization process of Ethylene Glycol (EG) based bio-lubricant from palm kernel oil. Palm Kernel Methyl Ester (PKME) was synthesized at a reaction time of 60 min, a molar ratio of oil: methanol 1:6, a temperature of 60 °C, and catalyst of 1 % wt/wt (in-situ transesterification) via reactive extraction. Box-Behnken design (BBD) in response surface methodology (RSM) was applied to this experimental layout. The effects of molar ratio, reaction time, and temperature on the synthesis of palm kernel bio-lubricant (PKBL) were evaluated. The PKBL structure was characterized by Fourier Transform Infra-Red (FT-IR) and Gas Chromatography-Mass Spectrometry (GC-MS) analysis, showing favorable lubricating properties. The PKME yielded 94.53 wt% based on the weight of the oil, while transesterification of the in situ derived PKME with EG yielded 93.08 wt% of the EG ester (Bio-lubricant). The maximum bio-lubricant recovery was 81.48 wt% obtained at a molar ratio of 3:1, time of 2.48 h, and temperature of 135 °C. The temperature and mole ratio were established to be the most significant terms. PKBL characteristics conformed to ISO VG criteria and had a high potential for bio-lubricant feedstock.

1. INTRODUCTION

Lubricants made of coal, petroleum, and natural gases are widely utilized [1]. As a result of their huge demand, it is necessary to seek other sources of producing lubricants [2]. Lubricants have received much attention from various industries including aviation, automobiles, machinery, etc. by performing vital applications such as elimination of wear particles, reduction of friction, increase of efficiency, uniform distribution of heat, and minimization of energy loss. Normally, lubricants are composed of 1–30 % performance-enhancing additives and 70–99 % base stock [3]. Schneider [4] reported that 50 % of these mineral-based lubricants were unrestricted in the environment during oil spills, disposal, and consumption. This lubricant is highly toxic and has poor biodegradability in the environment. Due to their long-term pollution effects coupled with mineral-based lubricant on the environment, it is necessary to use renewable and cheap feedstock for the production of bio-lubricants. Bio-based lubricants are also biodegradable and non-toxic in nature and, hence, cause little or no danger to the operators or the environment [5]. There are other sources of mineral-based lubricants such as animal fat or synthetic lubricants. However, lubricant produced from vegetable oil has produced better results due to their acceptable and favorable physical properties. Among the merits of bio-lubricants, lower coefficient of friction and high lubricity can be counted, compared to mineral-based lubricant. In addition, bio-lubricants have a high flash point, which makes them delay dissipation and evaporation when used in the environment

where the temperature is high [6]. Bio-lubricants enjoy some performance merits including low volatility, high shear stability, high viscosity indices, high dispersancy, high resistance to humidity, high detergency, and low compressibility [5]. In spite of these benefits, bio-based lubricants are still not broadly utilized due to some key disputes and complexities concerning their production and performance. Besides feedstock consistency, reliability, and industry recognition, bio-based lubricant also has two important negative physical properties: low thermal oxidative stability and poor low-temperature performance [7]. This is due to the presence of a double bond and β -hydrogen in the triacylglycerol ester responsible for this drawback. However, by using suitable chemical modification techniques including transesterification, selective hydrogenation, and epoxidation process, these two properties can be enhanced to make bio-based lubricants viable alternatives to mineral-based lubricants for diverse applications [8].

Transesterification of vegetable oil is more likely to produce a lubricant of appreciable fluidity with better temperature performance [9]. This method helps substitute the hydrogen atoms into the beta-carbon structures of the oil, leading to the formation of polyol ester. Various polyhydric alcohols utilized in transesterification of fatty acids methyl ester are ethylene glycol, trimethylolpropane, pentaerythritol, and neopentylglycol. Ethylene glycols are recognized to have a good branched structure and anti-freezing properties, which constitute the main properties of bio-lubricant production [10]. Bilal studied the application of ethylene glycol for the synthesis of bio-based lubricants using jatropha curcas oil as feed stock. This study utilizes the classical experimental design that changes one factor at a time and does not illustrate the interaction between process variables due to a large

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volume of laboratory experimental runs, making this approach time consuming. Hence, based on the reported compound model, the optimization of bio-lubricant production by reducing the number of experimental trials has received insignificant attention in this area of research [11].

In this study, a novel synthetic approach to transesterification reaction has been employed to produce palm kernel bio-lubricant of high yield. It is normally examined by optimizing the following reaction parameters including reaction temperature, reaction time, and mole ratio. In addition, the effect of variables and their interaction has been estimated by response surface methodology (RSM).

RSM is a flexible mathematical technique utilized in optimization, modeling, and experimental design [12]. It is an empirical modeling method that relates one or more responses to independent parameters. It gives statistical indicators on individual model terms and interactions [12]. It has been applied to the modeling of transesterification processes [13-16]. The fundamental methods for quantitative variables involve (a) fitting first-order (linear) or second-order (quadratic) functions of the predictors to one or more response variables and, then, (b) examining the characteristics of the fitted surface to decide what action is appropriate [17].

2. MATERIALS AND METHOD

2.1. Materials and reagents

The crude PKO utilized in this study was purchased from Bida town in Niger State of Nigeria. The instruments used include a two-neck round bottom flask, a density bottle, a viscometer, a magnetic heating stirrer, a thermometer, a measuring cylinder, and a separating funnel; in addition, the reagents such as ethylene glycol (EG), phenolphthalein, methanol (CHOH_4), sulphuric acid (H_2SO_4), and potassium hydroxide (KOH) were also employed in the study. The instruments mentioned above were all obtained from the Department of Agriculture and Bioresources Engineering, Federal University of Technology Minna, Niger State, Nigeria, while the reagents were obtained from Sigma-Aldrich (St. Louis), which were of analytical grade.

2.2. Methodology

2.2.1. Determination of flash point

In this part, 10 ml of oil sample was heated in a crucible to raise the temperature of the sample at a 5 °C interval. A thermometer was suspended in the sample with a retort stand. The flash point is the minimum temperature at which the vapor of the sample ignited when the flame was brought close to it [18].

2.2.2. Determination of pour point

Pour point is the temperature at which oil ceases to flow. The oil sample was chilled within a chilling bath to allow for the formation of oil crystal at 9 °C above the accepted pour point. For each 3 °C, the test jar was removed and tilted to check the exterior movement. When the sample ceases to flow while tilted, the jar was fixed in parallel for 5 seconds. As oil ceases to flow, there is a 3 °C increase in the corresponding temperature, and the result obtained was recorded as the pour point temperature in line with ASTM D97.

2.2.3. Determination of acid value

Then, 5 g of oil sample was placed in a conical flask of 250 ml; then, 50 mL of ether-ethanol solution was also added. The mixture was shaken properly; it was refluxed gently until the substance was completely liquefied. The solution was titrated with a sodium hydroxide titrant unit; pink coloration was observed after it persisted for 30 seconds. The used volume of sodium hydroxide titrant was measured, and the acid value was calculated according to Equation (1) [19].

$$\text{Acid Value} = \frac{\text{Titre Value} \times 5 \times 16 \times 0.00282}{\text{Weight of the sample}} = \frac{\text{MgKOH}}{\text{g}} \quad (1)$$

2.2.4. Determination of free fatty acid

Bravi et al. [20] reported that the free fatty acid (FFA) was determined by Equation (2).

$$\text{FFA} = \frac{\text{Acid Value}}{2} = \frac{\text{MgKOH}}{\text{g}} \quad (2)$$

2.2.5. Determination of viscosity

Oil sample was placed into a calibrated glass viscosity tube, as shown in Figure 1. It was allowed to settle down for 24 h and immersed in a warm bath at 40 °C (Figure 2). Then, the fluid sucks up a segment of the tube to the highest line on the right side of the tube, as shown in Figures 1 and 2. Once the oil meniscus strokes this line, a stop clock starts and continues until the oil meniscus strokes the lower line. This is then replicated three times in line with ASTM D445 -06.



Figure 1. Cannon viscosity experimental setup.



Figure 2. Experimental setup in progress.

2.2.6. Determination of specific gravity

The specific gravity of the oil was measured at 20 °C. The specific gravity bottle was weighted empty (W_1), filled with oil, and then reweighted (W_2). The difference between weights was divided by the weight of an equal volume of water, computed through the following Equation (3) [21].

$$\text{Specific Gravity} = \frac{W_2 - W_1}{W_3 - W_1} \quad (3)$$

where W_1 = weight of empty bottle, W_2 = weight of the oil content and bottle, and W_3 = Weight of water content and bottle.

2.2.7. Determination of saponification value

This method, previously explained by Bilal et al. [10], was used in this studied. Then, 5 g of oil sample was weighed to a flask; 50 mL of alcoholic KOH was slowly added from burette to the flask. A similar process was simultaneously considered, yet without adding the oil sample, coupled with air condenser to the flask. The contents were boiled gently on steam bath for about 1 h. The contents were allowed to be cooled at room temperature, and the inside of the condenser was rinsed with little distilled water and, then, the condenser was removed. The solution was titrated against 0.5 N HCL using phenolphthalein of 1 % wt/wt until the pink coloration was observed after changing into colorless. The difference between the titration values of the blank flask and the flask containing the oil was recorded, and the amount of KOH in mg (saponification value) was computed through Equation (4).

$$\text{Saponification Value} = \frac{28.05(V_0 - V_1)}{W} \quad (4)$$

where V_0 = Titre value of blank, V_1 = Titre value of the oil sample, and M = Weight of the oil sample used.

2.2.8. Determination of viscosity index

The viscosity index is calculated by ASTM method D2270-74 as follows:

$$\text{Viscosity index} = \frac{100(U-L)}{(L-H)} \quad (5)$$

where U = Viscosity of the sample at 40 °C, L = Viscosity of the sample at 40 °C of the VI=0 sample, and H = Viscosity of the sample at 40 °C of the VI=100 sample.

2.2.9. Synthesis of palm kernel methyl esters

This method was previously described by Matthew et al. [22]. The transesterification process of PKME synthesis is shown in Figure 3. Then, 300 g of oil sample was measured and transferred into a conical flask. The sample was preheated in a warm water bath of 65 °C; 2.5 g of KOH pellets (1 % wt/wt) was measured and liquefied in 100 g of methanol.

The methoxide (KOH + methanol) solution was inserted into the preheated oil in a 500 mL conical flask and positioned on a hot plate with a magnetic stirrer at a speed of 700 rpm. The reaction was set to run for 90 min and, then, terminated. At the end of the reaction, the mixture acquired was separated based on density variation by means of the separating funnel. Fraction of the PKME was washed with warm distilled water (70 °C) three times to remove the residuals that include catalyst, glycerol, soap, and methanol. The PKME was further dried using sodium sulfate.

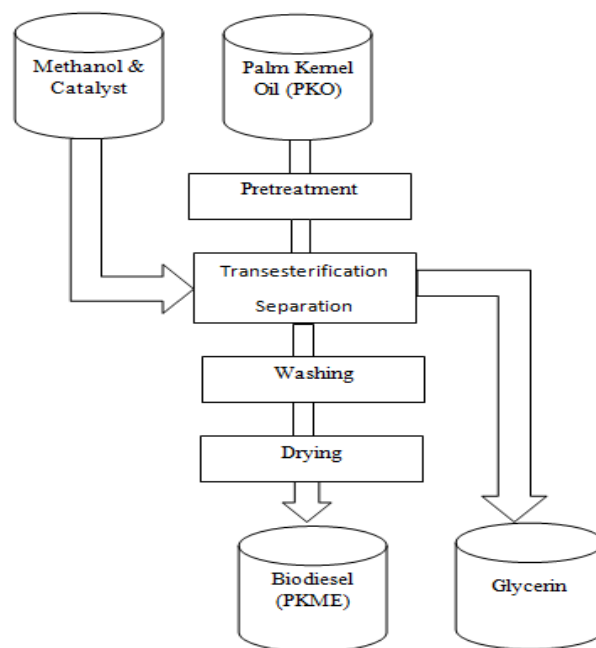


Figure 3. Schematic flow chart of palm kernel methyl ester production.

2.2.10. Synthesis of palm kernel bio-lubricant

Surapoj et al. explained this process [23]. By following the experimental layout in Table 1, a precise amount of PKME/EG ratio was measured into a round bottom flask of 250 mL, which was connected with a thermometer, water chilled reflux condensers, and a magnetic stirrer; 0.5 M sodium methoxide (prepared by liquefied sodium in 25 % of methanol) as a catalyst was added to the mixture. The reaction was conducted in a specific period of time and a temperature based on the design. At the end of the reaction, the mixtures were poured in a separating funnel and allowed to chill. The PKBL (Figure 4) was analyzed to determine its composition by gas chromatography, while Fourier Transform Infrared (FTIR) was also used to identify its functional group: viscosity index, flash point, viscosities, and pour point were also determined by proper analysis [22].

Table 1. Factors levels of independent variables for PKBL synthesis.

Independent variables	Low level (-)	Medium level (0)	High level (+)
Molar ratio	3:1	5:1	7:1
Temperature (°C)	60	100	140
Time (min)	30	90	150



Figure 4. Palm kernel bio-lubricant synthesis.

2.2.11. Design of experiment

RSM was employed to examine the input variables (PKME/EG ratio, reaction time, and temperature) that influence bio-lubricant yield through transesterification process, avoid repetition of experimental run, and utilize BBD to specify seventeen (17) experimental conditions applied to explore the effect of the three variables selected on PKBL yield (Table 2). The range of the variables explored are presented in Table 1 including PKME/EG ratio 3:1 to 7:1, time 30 to 150 min, and temperature 60 to 140°C. The three factors were assessed at high (+), low (-), and medium (0) levels. The pure error and lack of fit were estimated using five center points for the proposed model [24]. The coded value of the process parameter was determined by Equation 6 below:

$$x_q = \frac{x_q - X_t}{\Delta X} \quad (6)$$

where x_q is the coded value of the q th factor, X_q is the un-coded value of the q^{th} test variable, and X_t is the un-coded value of the q^{th} test factor at the center point. Second-order polynomial Equation (9) was utilized to express the bio-lubricant synthesis (Y) as a function of the independent variables.

$$Y = \partial_0 + \sum_{i=1}^p \partial_i X_i + \sum_{i<j}^p \partial_{ij} X_i^2 + \sum_{i<j}^p \partial_{ij} X_i X_j + e \quad (7)$$

where Y is the response factor (% yield), j and i signify quadratic and linear coefficients, respectively, e is the random number, p is the number of factors, ∂_i is the first-order model coefficient, and ∂_0 is the intercept. Multiple regressions were employed to fit the coefficients of the second-order polynomial models of the responses. The quality of the fitted quadratic polynomial responses model was evaluated by Analysis of Variance (ANOVA) and tests of significance. All RSM investigations were carried out by Statistica 7.0.1 software (Stat-Soft Inc., Tulsa, OK, USA).

Table 2. Box-Behnken design arrangement and response for PKBL synthesis.

Run	X ₁	X ₂	X ₃	X ₁ = Mole ratio	X ₂ = Tempt	X ₃ =Time	% Yield	Predicted value
1	0	+1	-1	5	140	0.5	74.83	86.86
2	0	0	0	5	100	1.5	82.13	91.33
3	-1	-1	0	3	140	1.5	89.43	89.36
4	0	0	-1	5	60	0.5	91.26	77.40
5	0	-1	0	5	100	1.5	83.96	91.43
6	0	+1	+1	5	140	2.5	84.25	85.13
7	-1	0	-1	3	100	2.5	85.78	86.43
8	0	0	0	5	100	1.5	80.31	85.24
9	-1	0	-1	3	100	0.5	93.08	91.83
10	0	-1	+1	5	60	2.5	81.56	76.56
11	+1	0	-1	7	100	0.5	85.78	79.83
12	+1	+1	0	7	140	1.5	78.48	83.67
13	0	-1	0	5	100	1.5	80.86	82.61
14	+1	-1	0	7	60	1.5	91.26	82.61
15	0	0	0	5	100	1.5	85.78	82.61
16	+1	0	+1	7	100	2.5	83.59	82.61
17	0	-1	0	3	80	1.5	85.78	82.61

Response surface was produced to find out the individual and interactive effects of the test factors on the bio-lubricant synthesis. The optimum value of the test variables was first obtained in a coded unit and, then, converted to an un-coded unit.

3. RESULTS AND DISCUSSION

3.1. Properties of crude palm kernel oil (CPKO)

The PKO was characterized for different physicochemical properties by standard techniques, while the values obtained are summarized in Table 3. The PKO was golden yellow in color at ambient temperature which is slightly different from that of the rubber seed oil [25] and ceiba pentandra seed oil [26]. This variance may be due to the solvents used in the extraction process. The density of PKO obtained was 970 kg/m³, showing that oil is lighter than water and also higher than the rubber seed oil [25], jatropha curcas L. oil [27], and ceiba pentandra oil and crude pangium edule [28]. According to [29], the recommended ranges of densities for a large marine four-stroke engine are 900 to 930 kg/m³. This means

that palm kernel is not acceptable. Even higher values, i.e., 991 kg/m³, are considered acceptable by Wartsila [29], which imply that palm kernel is not out of the question. The reflective index of the PKO was measured to be 1.49, which falls within the range documented in literature for organic oil (1.3 to 1.6) [30]. The viscosity of PKO was obtained to be 37.6 cSt, which is lower than jatropha curcas L. oil [27], yet higher than the conventional diesel (< 5 cSt).

The acid value of PKO was found 26±0.04 mg of KOH/g of oil, which is higher than the acid value of rubber seed oil (24±0.20 mg of KOH/g of oil) [25] and ceiba pentandra oil (15±0.12 mg of KOH/g of oil) [26]. The free fatty acid content of the PKO was found to be 13±0.02 %, which is higher than some seed oil such as ceiba pentandra oil [26] and rubber seed oil [25]. Iodine value is used to determine the degree of unsaturation in vegetable oil, methyl ester, and animal fat. The iodine value obtained in this study is 43.7 with a high degree of saturation. High iodine value has the propensity for polymerization, which results in deposit formation. Maximum iodine value of 125 is recommended for non-transesterified biofuel to be used in a large marine four-stroke diesel engine, while another major large engine manufacturer considers the

maximum iodine value of 120 [29]. It means that palm kernel can be used in this application.

3.2. Optimization of process variables for the yield of PKBL

3.2.1. Model fitting and analysis of variance (ANOVA)

To optimize the effects of transesterification reaction on palm kernel bio-lubricant synthesis, the BBD module in RSM was used. Multiple regression model was utilized to establish a

relationship among PKME/EG ratio, reaction time, and temperature as independent variables, while palm kernel bio-lubricant yield was considered as the response. The experimental data acquired from palm kernel bio-lubricant yield were employed to develop a model. The possibility of fitting the observed data to a statistical model is dependent on the interactions between cubic and quadratic functions and linear models as depicted in Table 4.

Table 3. Comparison of physicochemical properties of palm kernel seed oil with different seed oils.

Properties	Palm kernel oil [this study]	Rubber seed oil [25]	Jatropha curcas L oil [27]	Ceiba pentandra oil [26]	Crude pangium edule oil [28]
Moisture content (%)	-	-	-	-	-
Colour @ ambient temperature	Golden yellow	Golden yellowish	-	yellow	-
Refractive index	1.49	1.47	-	1.4705	1.4682
Density, kg/m ³ @ 24 °C	970	910	857.45	905.2 ^b	897.6 ^b
Calorific value, MJ/kg	-	39.34	39.8	-	39.52
Kinematic viscosity, Cst @ 40 °C	37.6	30 ^a	77.4	34.456	27.17
Free fatty acid, %	13±0.02	12.12±0.10	-	7.69±0.6	-
Cloud point, °C	16	3	11	-	-6
Iodine value	43.7	113	87.56	98	-
Pour point, °C	10	-1.5	4	-	-10
pH	-	-	-	-	-
Saponification value, mg of KOH/g of oil	346.82	235.58	-	224	-
Flash point, °C	143	-	-	-	-
Acid value mg, of KOH/g of oil	26±0.04	24±0.20	-	15.3±0.12	-

^a Measured @ 24 °C
^b Measured @ 40 °C

Table 4: Summary of P-values for PKBL synthesis.

Source	Sequential P-value	Lack of fit P-value	Adjusted R-square	Predicted R-square	Press	Remark
Linear	0.2136	0.0609	0.1178	-0.3960	518.93	Not Suggested
2FI	0.0176	0.1846	0.5648	0.0365	358.15	Not Suggested
Quadratic	0.0521	0.4805	0.7801	0.2560	276.58	Suggested
Cubic	0.4805	-	0.7797	-	-	Aliased

The adjusted R^2 and lack of fit, R^2 , and sequential p-value are predicted as 0.7801, 0.4805, 0.2560, and 0.0078, respectively; therefore, the quadratic model is used for the observed data. P-value less than 0.05 shows that the model is significant with a 95 % confidence interval [17]. Hence, for the model to be appropriate, lack of fit should also be non-significant [25]. The assessment between the pure and residual errors is known as lack of fit, which should be non-significant when the model is significant. The p-value for the interaction model is less than 0.05 with adjusted R^2 of an almost 60 % confident level while the lack of fit is significant; thus, it was not suggested and, instead, the quadratic model was selected. The quadratic polynomial model was used to predict the bio-lubricant synthesis in terms of coded values using experimental design as shown in Equation (10) excluding non-significant terms.

$$\text{Yield (\%)} = +117.34 - 0.0513X_1X_2 + 0.1195X_2X_3 + 0.96443X_1^2 \quad (8)$$

The analysis of variance (ANOVA) of the suggested model is presented and analyzed in Table 5. The model F-value is 7.31, implying that the model is significant and is validated by the P-value of 0.0078 [31]. Based on each significant term of linear coefficient (X_1 , X_2 , and X_3), interaction coefficient (X_1

X_2 , $X_2 X_3$, and $X_2 X_3$), and quadratic coefficient (X_1^2 , X_2^2 , and X_3^2) [32], it could be observed how efficiently the process variables affect the synthesis of bio-lubricant. $X_1 X_2$, $X_2 X_3$, and X_1^2 are the significant terms that affect the response variables. It can be concluded that the interaction coefficient is more significant in terms of linear and quadratic coefficients.

'Adeq Precision' measures the signal-to-noise ratio as higher than 4, which is desirable. The ratios of 8.811 indicate an adequate signal Russell [33]. This model can be employed to navigate the design space. The coefficient of variation was obtained as 2.67 %, showing a significant level of accuracy with the experimental data of the concluded model. The model fitness was validated using the R^2 value. For PKBL, the R^2 value obtained was 0.9038, showing that 90 % of variability in the response can be clarified by the independent variable. This entails that the prediction of experimental data was reasonably adequate [25]. In the regression model, when an independent factor has a positive sign, it signifies that an increase in the factor will cause an increase in the response, while a negative sign will result in a decrease in the response [33]. The combined increase of both molar ratio and temperature will lead to a decrease in the percentage yield, while that of temperature and time will result in an increase in the percentage yield.

Table 5. Analysis of variance for PKBL synthesis.

Source	Sum of squares	Df	Mean squares	F-value	P-value prob>F
Model	335.96	9	37.33	7.31	0.0078
X ₁ -Mole ratio	5.38	1	5.38	1.05	0.3390
X ₂ -Temp	18.03	1	18.03	3.53	0.1024
X ₃ - Time	3.74	1	3.74	0.73	0.4203
X ₁ X ₂	67.46	1	67.46	13.20	0.0084
X ₁ X ₃	6.52	1	6.52	1.24	0.2957
X ₂ X ₃	91.36	1	91.36	17.88	0.0039
X ₁ ²	62.66	1	62.66	12.27	0.0100
X ₂ ²	0.22	1	0.22	0.042	0.8427
X ₃ ²	1.49	1	1.49	0.29	0.6064
Residual	35.76	7	5.11		
Lack of fit	15.29	3	5.10	1.00	0.4805
Pure error	20.47	4	5.12		
Cor total	371.72	16			

Std. Dev. = 2.26; mean = 84.60; C.V. = 2.67 %; PRESS = 276.58; R-Squared = 0.9038; Adj R-Sq = 0.7801; Pred R-Sq = 0.2560; Adeq precision = 8.811.

R-Squared = 0.9038; Adj R-Sq = 0.7801; Pred R-Sq = 0.2560; Adeq precision = 8.811.

3.2.2. Effect of process parameter on transesterification reaction

The interaction among the three variables examined for PKBL synthesis was considered by 3D surface plot (Figures 5 to 7), providing a chance to make visual observations.

3.2.3. Effect of temperature and molar ratio

Figure 5 shows the combined effects of temperature and molar ratio on PKBL synthesis while reaction time was kept constant. Temperature varied from low to high values of 80 °C and 140 °C, molar ratio varied from 3:1 to 7:1, while time was kept constant at 150 min. It was observed that the conversion of PKBL synthesis increased as the temperature and molar ratio increased [17]. At low values of temperature and molar ratio, a PKBL yield of 80.56 wt% was obtained, in which the pattern followed a quadratic path and was inconsistent with the pattern of previous research [17]. However, low temperature and high molar ratio were combined, leading to a yield of 84.52 wt%, while high temperature and low value of molar ratio yielded an increase up to 93.08 wt %. Based on the surface plot, it was observed that the PKBL conversion increased as PKME concentration increased. Therefore, the maximum PKBL conversion was obtained for the low mole ratio, resulting from the stoichiometry of transesterification and requiring a 3:1 ratio for PKME and EG, since the reaction involves the formation of one ester and alcohol with another ester and alcohol [17]. This shows that temperature has significant effect on the yield. However, the interaction between high temperature and low molar ratio value gave better yield than that of reverse of about 9 wt% increment; then, it can be proposed that temperature shows significant effects than the molar ratio.

3.2.4. Effect of reaction time and molar ratio.

The effect of PKME/EG ratio and reaction time on the yield of PKBL at a constant temperature is depicted in Figure 6 by 3D plot. The PKME/EG ratio varied from 3:1 to 7:1; reaction time also varied between 30 and 150 min while keeping the process temperature constant at 90 °C. The plot shows the interaction that occurs between the PKME/EG ratio and reaction time with significant effect on PKBL synthesis. The PKBL yield was high at a low PKME/EG ratio and reaction time. It is obvious that the quantity of PKBL yield increases

with a decrease of PKME/EG ratio. Thus, an excess of PKME could be used to drive the reaction to near completion. Consequently, the PKME concentration results in a greater PKBL conversion within a shorter time [17]. The mole ratio (PKME/EG) is a fundamental variable in the transesterification process for bio-lubricant synthesis [34]. Although the effects of the reaction time were not so manifest like that of the PKME/EG ratio; hence, the PKBL yield increased with reaction time. The PKBL yield increased from 74.83 wt % to 89.50 wt % in this work, and maximum bio-lubricant was observed at a reaction time of 2.50 H.

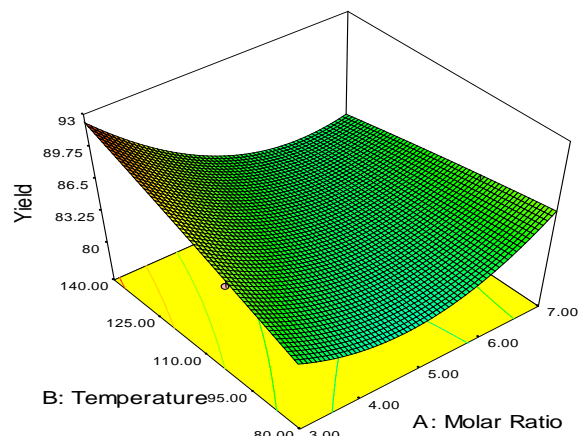


Figure 5. 3D surface response plot between molar ratio and temperature against PKBL yield.

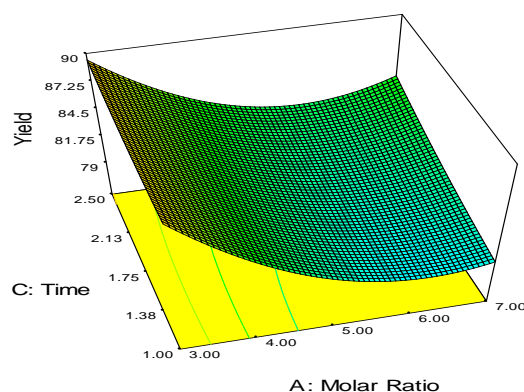


Figure 6. 3D surface response plot between reaction time and molar ratio against PKBL yield.

3.2.5. Effect of temperature and time.

Figure 7 shows the effect of reaction time and process temperature on the yield of PKBL at a fixed molar ratio. The time of the reaction decreased from 150 to 30 min, while the process temperature increased from 60 to 140 °C keeping the PKME/EG ratio constant at 5:1. The quantity of PKBL yield increased as the process temperature enhanced due to the increasing affinity of PKBL with the EG at high temperatures along with a higher mass transfer rate [32]. Due to the increasing temperatures, the EG viscosity was reduced and the solubility of PKBL in EG enhanced. Hence, decreased EG viscosity and increased EG function at high temperatures can improve the transesterification process, although the effects of the reaction time were not so obvious like that of the process temperature. An increase in reaction time does not improve the catalytic activity at low temperatures. Meanwhile, high temperatures improved the dispersion of catalyst particle in liquid medium with better mass transfer between the reactants [17].

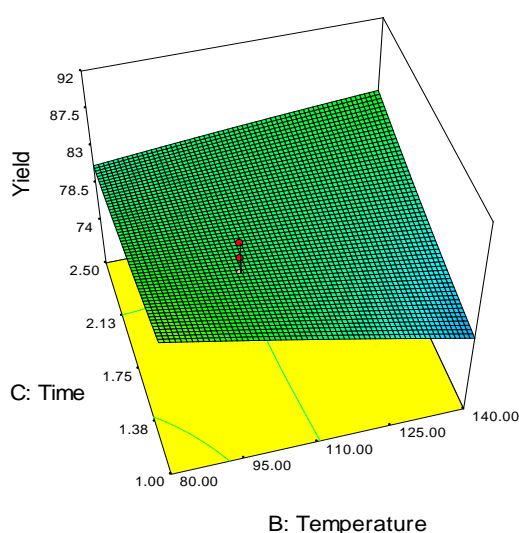


Figure 7. 3D surface response plot between time and temperature against PKBL yield.

3.3. Process variable optimization

Table 6 illustrates the optimum result of PKBL yield. The predicted response was generated by using a point prediction node (under optimization node in the BBD module). PKBL/EG ratio temperature and reaction time were all fixed in the range of 3:1–7:1, 60–140 °C, and 0.5 – 2.5 H, respectively. PKBL yield was maximized in the process condition of 74.83–93.08 wt%. Based on these criteria, the software decided (Table 6) the following optimum condition: PKME/EG of 3:1, temperature of 135 °C, time of 2.48 H, and yield of 81.46 wt% at a desirability value of 1.00.

Table 6. Optimization results for PKBL synthesis.

Parameters	Optimum operating condition
Molar ratio	3:1
Temperature (°C)	135
Time (H)	2.48
Yield (optimum) wt%	81.48

3.4. FT-IR analysis

The chemical composites of EG, PKBL, and PKME were analyzed using FTIR, and results are shown in Figure 8. The

FTIR spectrum of PKBL and PKME shows absorption bands at 1741.59 cm^{-1} and 1743.96 cm^{-1} , respectively. These absorption bands result from the C–O and C=O stretching vibrations in ester, which led to proving the presence of oxygen in PKBL and PKME [17]. Based on the figure, peak of hydroxide group at 3326 cm^{-1} was found in EG, which is very small and can be neglected in PKBL (b); accordingly, it is shown that the bio-lubricant esterification reaction is considerably close to completion. A similar observation has been reported for FTIR elsewhere [35].

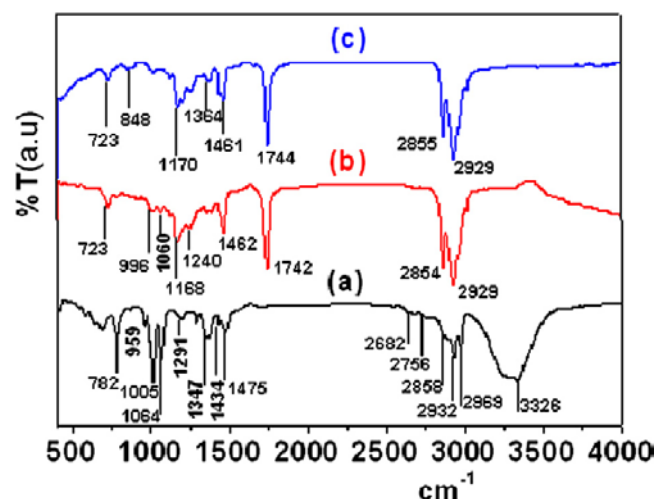


Figure 8. IR spectra of (a) EG (b) PKBL (c) PKME.

There was also an observed shift in the wavelength of 1543.1 cm^{-1} for the spectrum of carboxylic acid functional group to 1742.74 cm^{-1} for the spectrum of EG ester. This is quite related to the work of Arbain and Salimon [35].

3.5. GS-MS analysis

The results of the fatty acid composition of palm kernel and jatropha oil bio-lubricant are shown in Table 7. The composition of fatty acid in the bio-lubricant produced was 2.35 %, which is higher than that reported by Arbain and Salimon [35]. This may be due to the difference in feed stock and variation in experimental conditions.

Table 7. Comparisons of composition of PKBL with Jatropha bio-lubricant.

Products	Percentage (%) [this study]	Percentage (%) [24]
Fatty acid	2.35	0.5
Monoester	0.82	-
Diester	1.50	0.9
Triester	95.33	98.6

However, the fatty acid consists mainly of ricinoleic acid with favorable lubricating properties and can improve the properties of the bio-lubricant. The percentage of monoester (ME) is quite low (0.82) due to rapid reaction that takes place in the conversion of ME to diester (DE). However, the rate of conversion of DE to TE is lower than that of ME to DE; thus, the percentage of DE is higher (1.50) than that of ME. As the reaction proceeds, DE is converted to Triester (TE), which is the desired product composition in bio-lubricant. Composition of TE was 95.33 %, which is higher than that reported by Ghazi et al. [36] at 90 % composition of TE and lower than 98.6 % reported by Arbain and Salimon [35].

3.6. Bio-lubricant characterization results

The physicochemical properties of the PKBL were compared with other plant seed bio-lubricants and ISO viscosity grades, as presented in Table 8. The viscosity of the palm kernel oil-based bio-lubricant was determined to be 32.67 and 6.10 Cst at 40 and 100 °C, respectively, which are quite different from that of sesame [17], rapeseed [17], and jatropha [9]. These variations may be attributed to differences in the fatty acid profile of the base oil or the process conditions/catalytic modification techniques used.

These results showed that there was a remarkable improvement in the viscosity of palm kernel oil methyl ester upon transesterification with EG. The value obtained shows that the bio-lubricant synthesized meets the ISO viscosity grade requirement [10]. The findings depict that palm kernel polyol ester (bio-lubricant) has potential applications as gear oil in automobile, since its properties conform to [11] and [9] requirements for this type of lubricant. There are three standard specifications for lubricants of which ISO viscosity grade [11] is one of them and represents over 80 % of all lubricants consumed [10].

Table 8. Properties of PKBL and comparison with other seed oil bio-lubricant, and ISO viscosity grades.

Properties	Pour point (°C)	Flash point (°C)	Viscosity @40 °C CSt	Viscosity @100 °C CSt	Viscosity index
PKBL	-6	216	32.67	6.10	232
CPKO	10	143	37.6	4.78	196
Sesame biolube [17]	-21	196	35.55	7.66	193
Rapeseed biolube [17]	-15.5	-	35.34	7.99	209.2
Jatropha biolube [9]	-8	215	45.3	9.21	191
ISO VG32 [10]	<-10	204	>28.80	>4.10	>90
ISO VG46 [11]	<-10	220	>4.40	>4.10	>90
ISO VG68 [11]	<-10	226	>61.40	>4.10	>198
ISO VG100 [17]	<-10	246	>90	>4.10	>216
ISO VG220 [9]	-6	265	>12	>4.10	>50

Viscosity index (VI) shows the behavior of the lubricant at different temperatures. PKO-based oil synthesized lubricant was characterized by a high VI of 232, as shown in Table 8. This exceptionally good VI value obtained was higher than the values reported by Mohammed et al. [37], rapeseed [17], and jatropha [9]; however, it was lower than the value of Phani [16]. High VI permits lower wear and lubricant consumption during its application. Lubricants with higher VI (>130) find a wide variety of applications [37]. The result indicates that the higher the VI is, the less significant the viscosity variation of the synthesized palm kernel-based oil lubricant will be.

Pour point is the property of bio-lubricant that determines its low temperature usability. The palm kernel derived bio-lubricant has a pour point of -6 °C, which is a considerable improvement from 10 °C, compared with the PKO that reacted with the EG. This improvement is one of the properties imparted on the PKME upon reacting it with a branched polyol (EG). Arbain and Salimon [35] stated that a higher degree of branching of esters led to low pour points, which are desirable properties of a lubricant.

Flash point is the lowest temperature at which a lubricant gives off enough vapor to form an ignitable mixture with the air. It is used for the assessment of the hazardous potential of a lubricant. The result of the analysis in Table 8 shows that the flash point of ester EG produced was 216 °C. The high flash point indicates the safety of the resulting ester of EG. The value also shows high consistency with the reported literature of Musa et al. [9].

4. CONCLUSIONS

This study showed that palm kernel oil had the potential to produce biodegradable lubricant using reactive extraction. The experimental result of bio-lubricant produced showed that EG ester exhibited favorable characteristics. FTIR analysis results showed the absence of OH group of EG and presence of EG ester. Complimentary GC-MS analysis results showed that high value of triester (95.33 %) was obtained after chemical

modification depicting the effectiveness of the conversion process. The EG esters of palm kernel oil produced showed quantitative agreement with ISO viscosity grade requirement and established its potential usage as light gear oil. BBD module in RSM was effectively selected for maximizing the reactions parameter of PKBL synthesis. The effects of PKME/EG ratio, reaction time, and process temperature on the PKBL synthesis were also examined and optimized. The model predicts the optimum condition for the selected transesterification variable at a PKME/EG ratio of 3:1, a reaction time of 2.48 h, and a process temperature of 135°C with a predicted PKBL yield of 81.46 wt%. The ANOVA entailed that PKME/EG ratio and process temperature were the most significant factors that affected the bio-lubricant yield.

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