PROCESS OPTIMIZATION AND KINETICS OF BIOLUBRICANT SYNTHESIS FROM FLUTED PUMPKIN SEED

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Abstract

Fluted pumpkin biolubricant (FPBL) was synthesized by transesterification of fluted pumpkin methyl ester (FPME) and trimethylolpropane (TMP) using calcium hydroxide, $Ca(OH)_2$ catalyst. First and second order kinetic models were analyzed to choose the optimum one regarding their relative simplicity and accuracy of fitting the experimental data obtained at different operating conditions. The second order kinetic model gave the best fit to the experimental data with an overall rate constant of 2.05×10^{-1} (%wt/wt min ◦C)$^{-1}$ and a regression value of 0.958. The kinetic energy for the synthesis of FPBL was estimated to be 40.65 kJ/mol. Response Surface Methodology (RSM) via Central Composite Design (CCD) was used to carry out the optimization of the transesterification process. The optimum conditions for the yield of TMP triester were 160°C, 6 h reaction time and a mole ratio (MME:TMP) of 6:1 at which the triester yield was 81.42%. The properties of FPBL met the requirement for ISO VG32 and VG46 viscosity grades, and were found comparable to other plant based biolubricants such as palm oil and calophyllum oil biolubricants.

Keywords: Fluted pumpkin, biolubricant, transesterification, kinetics, optimization

Introduction

Lubricants have wide applications in industries, automobiles and aviation machinery by performing crucial functions such as reducing friction, removal of wear particles, increasing efficiency, minimizing energy losses and uniform distribution of heat. Generally, lubricants are composed of 70–99% base stock and 30–1% performance-enhancing additives (Borugadda & Goud, 2015). Therefore, the basic properties of a lubricant such as oxidative stability, low-temperature flow properties and lubricity are mainly determined by the base oil. A vast majority of the conventional lubricants are mineral oil-based and are primarily obtained from petroleum derivatives.

About 50 percent of these mostly mineral based lubricants are released into the environment during use, spills, and disposal (Schneider, 2006). These lubricants have poor biodegradability and are highly toxic to the environment (Horner, 2002). Strong environmental concerns and rising regulations over contamination and pollution in the environment have increased the need for renewable and biodegradable lubricants (Fox & Stachowiak, 2007). The nature of vegetable oil, that is, easily renewable, biodegradable and non-toxic makes it the best alternative to mineral oil in the production of lubricants (Syaima et al., 2014). It also possesses the properties required for proper lubrication, including excellent lubricity, high flash point and viscosity index, as well as good viscosity (Ishak & Salimon, 2013). However, some vegetable oils have some undesirable properties which limit their application as industrial lubricant. Such properties include high pour point, low thermal and oxidative stabilities. The low oxidative stability is caused by the carbon-carbon double bond in the fatty acid chain and beta hydrogen on glycerol vulnerable to oxygen assault (Widyawati et al., 2014).

Chemical modification of vegetable oil, by exchanging the glycerol molecule with trimethylolpropane (TMP) resulting in the formation of a typical synthetic (TMP) ester, has been applied to overcome the limitations of plant oils and further enhance the oil's stability (Fox & Stachowiak, 2007; Ishak & Salimon, 2013; Gunam Resul et al., 2012). Synthetic esters, like TMP esters, have been used for many years as base lubricating fluids due to their environmental friendliness, notwithstanding their high market value. They are also known for their excellent lubricating properties such as good thermal and oxidative stability, low volatility, high viscosity index and excellent low temperature fluidity (Ishak & Salimon, 2013).

TMP esters can be synthesized by the esterification of fatty acids of vegetable oils with TMP in the presence of an acid catalyst. Alternatively, fatty acid methyl esters (FAMEs) can be transesterified with TMP using a base catalyst to yield TMP esters. The latter process gives a higher TMP ester yield than the former. A previous study reported on the esterification of rubber seed oil (RSO) fatty acid and TMP showed that RSO was successfully converted to TMP ester with 78% of triesters at a temperature of 150 °C using 2% (w/w) of sulphuric acid catalyst at 5 h reaction time (Salimon & Ishak, 2011). In another study reported on the transesterification of palm oil methyl ester (POME) with TMP using 0.8% (w/w) of sodium methoxide, palm oil TMP ester containing 98% of triester was successfully synthesized in less than an hour (Yunus et al., 2003). Other vegetable oils such as jatropha, rape seed, soybean and palm kernel oil have been used in the synthesis of TMP esters.

Fluted pumpkin seed oil (FPSO) has good potential for the synthesis of TMP esters. It is rich in unsaturated fatty acids, comprising up to 80.26% of its fatty acid composition (Bello et al., 2011). The major fatty acid found in FPSO is linoleic acid (C18:2), with a total percentage of 64.41%. Other unsaturated fatty acids found in it are oleic acid (C18:1) comprising 13.42% and eicosapentanoic acid (C20:5) comprising 2.43%. The only saturated fatty acid found in FPSO is palmitic acid (C16:0) comprising 19.74% of the oil (Bello et al., 2011). The high percentage of unsaturation in FPSO gives the oil a low pour point which is necessary for efficient performance of a lubricant in all climatic conditions especially in a winter environment. FPSO also has a high viscosity which is necessary for efficient lubrication of contact surfaces. This work studied the kinetics of the transesterification reaction between FPME and TMP, using $Ca(OH)_2$ catalyst, for the synthesis of TMP esters. The best kinetic model for the transesterification reaction was chosen based on its accuracy of fitting the experimental data obtained at different operating conditions. The optimization of TMP triester yield was also carried out using response surface methodology (RSM). RSM was chosen in this study because it provides functions for generating standard designs (currently, central-composite design and Box-Behnken design). It also provides means of visualizing a fitted response surface, in addition to providing guidance for further experimentation, for instance, along the path of steepest ascent (Russell, 2009).

Materials and methodology

Materials

Fruit pods of fluted pumpkin seed (*Telfairia occidentalis Hook F.*) were purchased from Eke Awka market in Anambra State, Nigeria. Trimethylolpropane (1,1,1-Tris(hydroxymethyl)propane dist., ≥ 98.0% (GC)) was purchased from Aldrich-Zigma. Other reagents were of analytical grade.

Experimental procedure

TMP esters of fluted pumpkin were synthesized via a two-step transesterification process as shown in the flow chart in Figure 1.

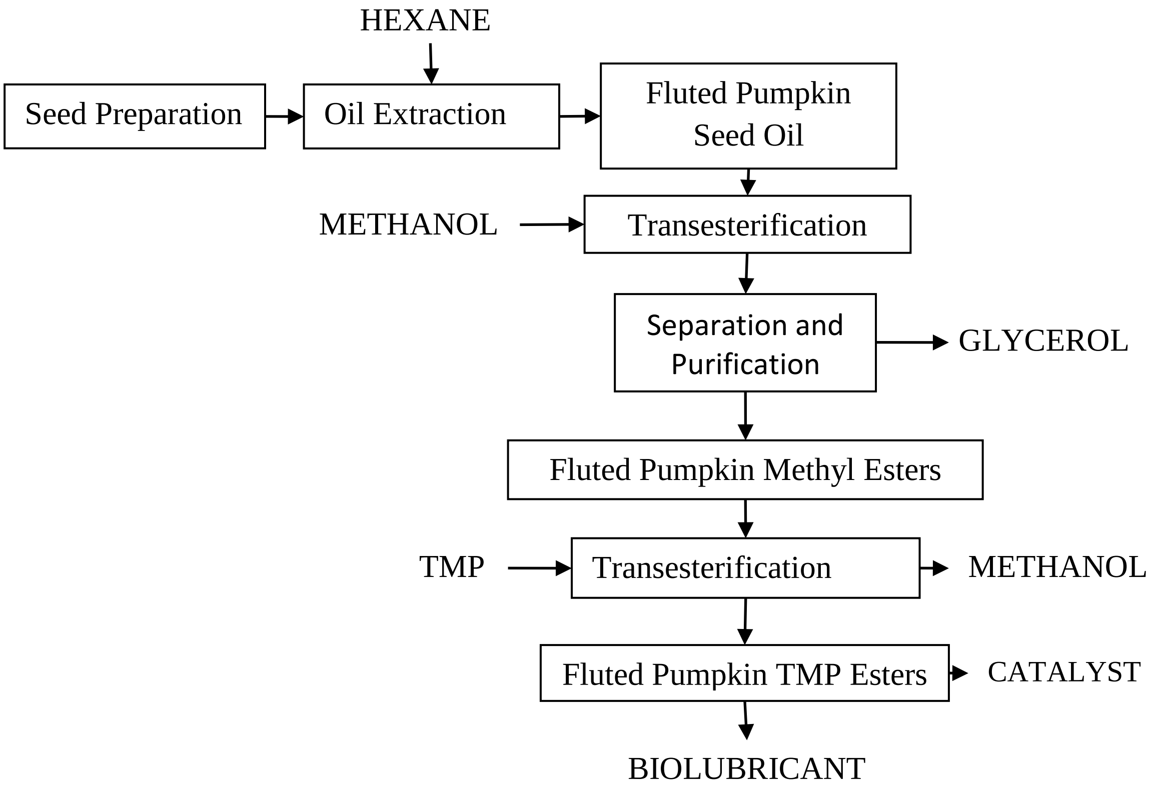
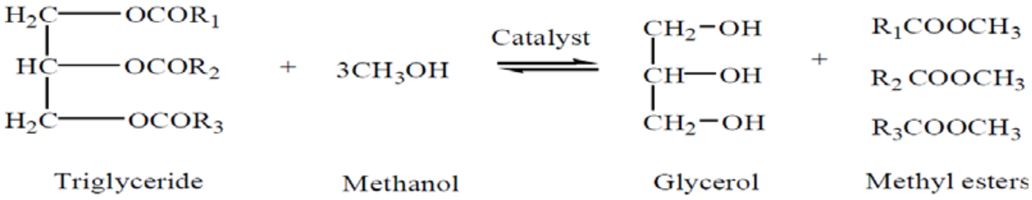
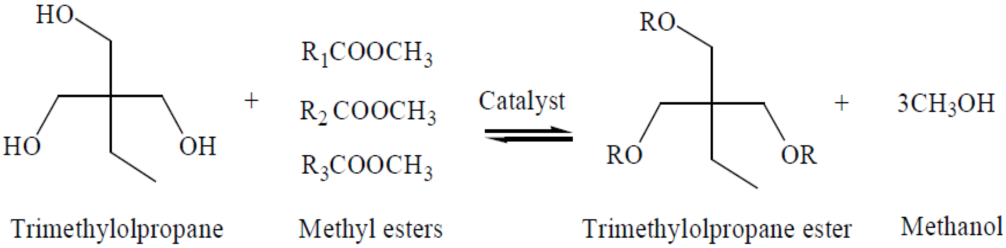


Figure 1: Simplified flow diagram for the synthesis of FPBL

The FPSO extracted from fluted pumpkin seeds was first transesterified with methanol to yield FPME as shown in Equation 1. The by-product, glycerol was separated from FPME using separating funnel and the FPME was subsequently purified by washing, and dried by heating. The purified FPME was transesterified with TMP to produce TMP esters as shown in Equation 2. The procedure for the reaction was modified from Surapoj et al. (2013). The reactor consists of a 500-mL three-necked round bottom flask equipped with a water-cooled reflux condenser, a CO_2 line and a magnetic stirrer. A thermostatic hot plate was used to control the reaction temperature. Typically, 10 gm of TMP was introduced to the flask and then melted by heating to 110 °C with continuous stirring under CO_2 flow. The temperature was maintained at 110 °C for about 10 min to remove moisture from the TMP due to its hygroscopic nature. A calculated amount of FPME according to the respective FPME:TMP mole ratio was subsequently introduced into the reactor and the resulting mixture was heated to the desired temperature before adding the catalyst ($Ca(OH)_2$). Samples were taken at specific intervals during the experiment for analysis. The product mixture was cooled to room temperature by an ice bath after the reaction course. The solid catalyst was then separated from the product mixture by filtration.





Gas chromatography analysis

The samples compositions were determined using a Buck 910 Gas Chromatograph. The temperature program involved holding at 80 ^{o}C for 2 min, then heating to 340 ^{o}C at 5 ^{o}C /min, and then finally holding at 340 ^{o}C for 5 min. The injector was held at 300 ^{o}C, while the detector was held at 360 ^{o}C. A split-ratio of 1:10 was employed. The run-time for each analysis was 45 min. This ensured smooth peaks and proper elution of the ester products. The solutions for GC injections were prepared by dissolving 1mL of the product sample in 5 mL of ethyl acetate solvent and warmed in a water bath at 60 ^{o}C for 15 min before injection into the chromatograph. 15 µL of injection volume was used in each run.

Establishment of kinetic model

The effect of temperature and time on the reaction was employed in the development of the kinetic model for the transesterification of FPME with TMP. The kinetics was based on the decreasing rate of the concentration of TMP, the limiting reactant (Gunam Resul et al., 2012; Nurdin et al., 2015).

Optimization using Central Composite Design

The CCD was used to study the effects of the variables on their responses and subsequently in the optimization studies. This helps to optimize the effective parameters with a minimum number of experiments, and to analyze the interaction between the parameters. Batch experiments were conducted based on the CCD to analyze the effects of temperature, mole ratio and reaction time, on the yield of trimethylolpropane triester. The range and levels of individual variables for the design are given in Table 1. A statistical program package, Design Expert 8.7.0.1 was used to carry out regression analysis of the data obtained and to estimate the coefficient of the regression equation. ANOVA analysis was used to validate the regression equation. Response surfaces were drawn to determine the individual and interactive effects of the test variables on the yield of TMP triester.

Table 1: Factors levels of independent variables for TMP triester yield

Independent Factors	-α	Low level (-)	Medium level (0)	High level (+)	+α
Temperature (^oC)	133.18	140	150	160	166.82
Time (hours)	3.32	4	5	6	6.68
Mole ratio	3.318	4	5	6	6.68

Results

Kinetic study

The analysis of the product formation and the depletion of the limiting reactant was carried out to determine the best kinetic model for the transesterification reaction. The reaction follows the scheme as given below:

$$\mathrm{FPME} + \mathrm{TMP} \rightleftharpoons \mathrm{ME} + \mathrm{M} \qquad (3)$$

$$\mathrm{FPME} + \mathrm{ME} \rightleftharpoons \mathrm{DE} + \mathrm{M} \qquad (4)$$

$$\mathrm{FPME} + \mathrm{DE} \rightleftharpoons \mathrm{TE} + \mathrm{M} \qquad (5)$$

Overall reaction:

$$3\mathrm{FPME} + \mathrm{TMP} \rightleftharpoons \mathrm{TE} + \mathrm{M} \qquad (6)$$

where M is methanol, ME is monoester, DE is diester and TE is triester. The kinetics study was carried out during the first 50 min of the reaction. The stoichiometric mole ratio between FPME and TMP is 3:1, but excess FPME was used to promote forward reaction since the transesterification reaction is a reversible reaction. Hence, TMP was considered as the limiting reactant. A simple kinetic approach was adopted in this study by discarding the intermediates. The rate constant, K_{TMP}, was based on the decreased rate of TMP concentration (Gunam Resul et al., 2012).

Therefore, the rate law is given by:

$$\left[\frac{1}{\mathrm{TMP}}\right] = \mathrm{K}_{\mathrm{TMP}}\mathrm{t} + \left[\frac{1}{\mathrm{TMP}_0}\right] \qquad (7)$$

where [TMP] is the concentration of TMP at time, t, K_{TMP} is the second order rate constant with respect to [TMP], and $[TMP_0]$ is the initial concentration of TMP. The first and second order kinetic models were investigated using the plots in Figures 2 and 3. The reaction rate constants at different temperatures with their corresponding regression (R^2) values are presented in Table 2. The regression values for the second order kinetic plot were found to be higher than those of the first order for all considered temperatures. Therefore, second order kinetic model was chosen as the best kinetic model for the transesterification of FPME with TMP. The overall rate of the second order kinetics was deduced from the plot in Figure 4, and compared in Table 3 with the values obtained from other studies. Figure 4 shows that increase in temperature resulted in increase in the rate of reaction. However, no significant increase was observed when the temperature was increased from 150 to 160 °C, possibly due to the rapid consumption of TMP on which the kinetics was based on. The figure also confirmed that the reaction actually follow the second order kinetic model. The overall rate constant obtained for the synthesis of FPBL was 2.05×10^{-1} (%wt/wt min ◦C)$^{-1}$.

Gunam Resul et al. (2012) reported that the synthesis of jatropha biolubricant using sodium methoxide catalyst followed an overall second order kinetic model with a rate constant of 1.80×10^{-1} (%wt/wt min ◦C)$^{-1}$, while Nurdin et al. (2015) reported that the synthesis of jatropha biolubricant using paphiaundulata shell waste catalyst followed an overall second order reaction with a rate constant of 4.27×10^{-02} (%wt/wt min ◦C)$^{-1}$.

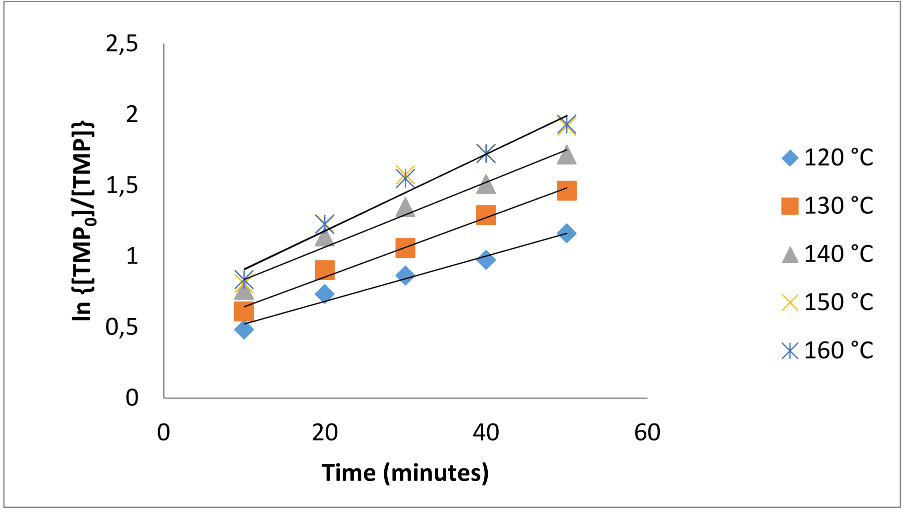


Fig. 2: First-order kinetics plot for the synthesis of FPBL

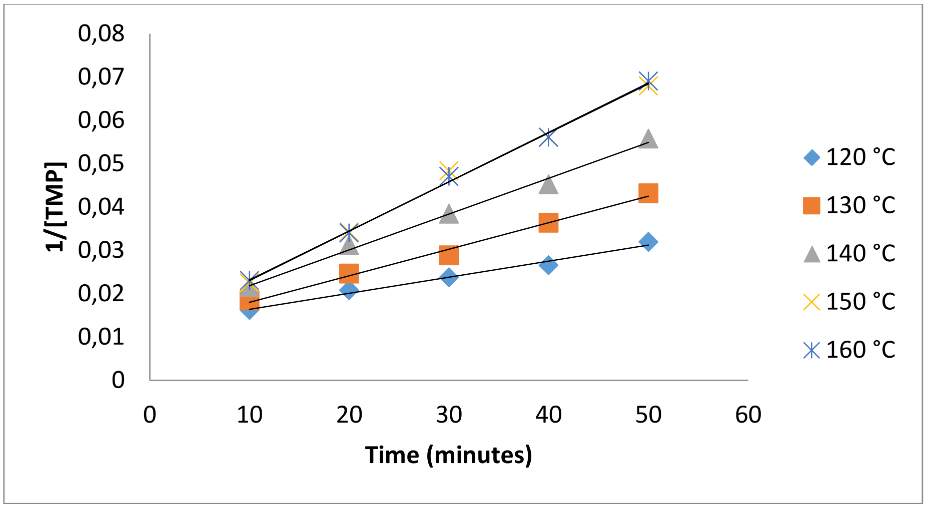


Fig. 3: Second order kinetics plot for the the synthesis of FPBL

Table 2: Reaction rate constants and regression values at various temperatures

Temperature (°C)	First order		Second order	
	$K_{TMP,\ 1st}$ (%wt/wt min)$^{-1}$	R^2	$K_{TMP,\ 2nd}$ (%wt/wt min)$^{-1}$	R^2
120	1.6E-02	0.979	3.70E-04	0.985
130	2.0E-02	0.990	6.10E-04	0.992
140	2.4E-02	0.980	8.20E-04	0.994
150	2.7E-02	0.955	1.12E-03	0.993
160	2.7E-02	0.972	1.14E-03	0.997

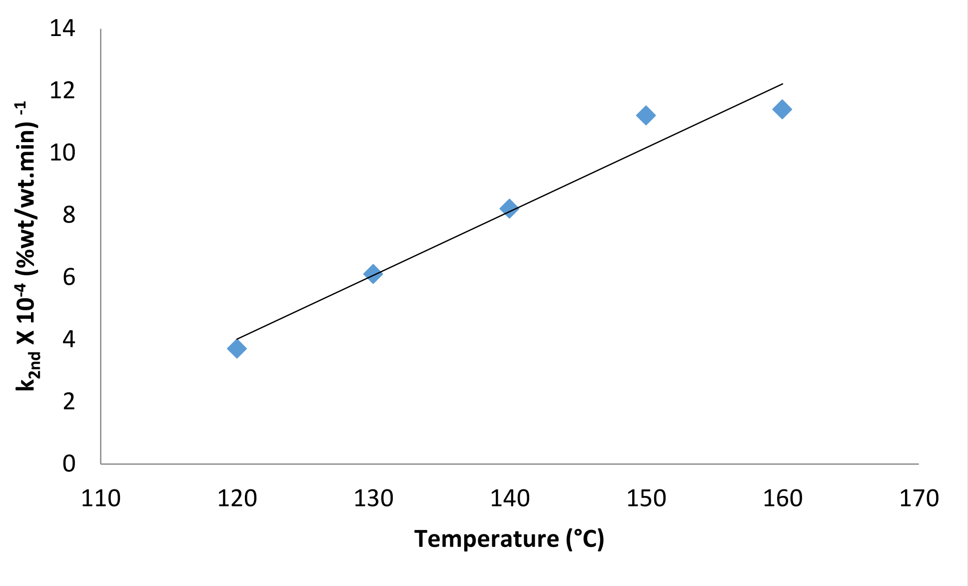


Fig.4: Overall second order kinetics model for the synthesis of FPBL at various temperatures

Table 3: Overall rate constant for second order reaction kinetics model

Biolubricant	Catalyst	Overall 2nd Order rate, K_{TMP} (% wt/wt min °C)$^{-1}$	R^2
This work	Calcium hydroxide	2.05E-01	0.958
Jatropha[a]	Sodium methoxide	1.80E-01	0.888
Jatropha[b]	Paphiaundulata shell waste	4.27E-02	0.987

[a] Taken from Gunam Resul et al. (2012).
[b] Taken from Nurdin et al. (2015).

Activation energy

Activation energy is the amount of energy required for a reaction to take place. Rate constant has been known to be dependent on activation energy. The dependency of the rate constant, k on temperature should fit the Arrhenius equation:

$$\log_{10} K = \frac{-E_a}{2.303RT} + \log_{10} A \qquad (8)$$

where R is the gas constant (R = 8.314 J K^{-1} mol^{-1}) and T is temperature in Kelvin (Gunam Resul et al., 2012). The activation energy, E_a was calculated from the slope of the plot of $\log_{10}$ k against 1/T in Figure 5. The calculated value of the activation energy for the synthesis of FPBL is compared with those of other plant based biolubricants in Table 4.

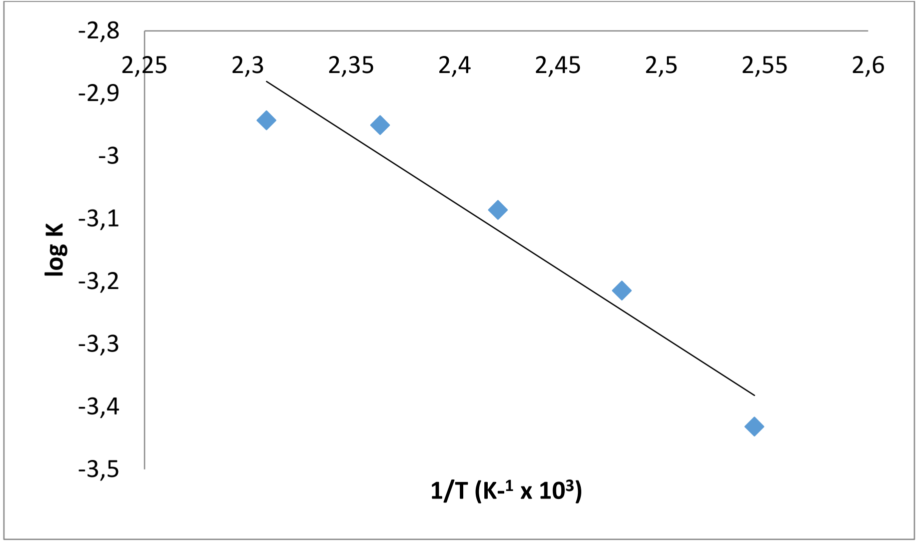


Fig. 5: Activation energy plot for the synthesis of FPBL

Table 4: Activation energy for the synthesis of FPBL in comparison with other biolubricants

Biolubricant	Activation Energy (kJ/mol)	R^2
This work	40.65	0.936
Jatropha[a]	1.650	0.861
Palm oil[b]	140.58	0.985

[a] Taken from Gunam Resul et al. (2012).
[b] Taken from Yunus et al. (2003).

The estimated activation energy for the transesterification of FPME with TMP was about 41.40 kJ/mol. If a reaction has a high activation energy, the rate of the reaction may be infinitesimally slow. The low activation energy of this reaction implies that the reaction occurs almost readily at designated temperatures. The activation energy for the synthesis of jatropha and palm oil biolubricants were reported to be 1.65 kJ/mol and 140.58 kJ/mol, respectively. Fluted pumpkin, jatropha and palm oil biolubricants were all synthesized by transesterification of their methyl esters with TMP, hence the comparison. However, transesterification of palm oil biolubricant was carried out at lower temperatures, ranging from 70 to 100 °C. The values of activation energy for fluted pumpkin and jatropha biolubricants were lower because their reactions took place at higher temperatures and therefore were less sensitive to temperature changes as compared to that of palm oil. Changes in temperature resulted in little changes in reaction rate for fluted pumpkin and jatropha, while increase in temperature resulted in significant increase in the rate of reaction for palm oil.

Optimization process using Response Surface Methodology

The product of the transesterification reaction consists of several components which include monoester, diester, triester and unconsumed FPME. It was known, prior to the experiments, that the reaction would be a step-wise process whereby intermediates (monoester and diester) would be formed before the desired product, triester, would be finally produced (Gunam Resul et al., 2012). High composition of triester is required to produce a lubricant with good lubrication properties because it improves the viscosity and thermal properties of the lubricant (Salimon & Ishak, 2011).

The optimization process for the yield of triester, in the synthesis of FPBL was carried out using CCD. Three important factors which are temperature, time and FPME:TMP mole ratio were used as the independent variables where their combined effects were examined. The percentage yield of triester was the dependent variable or the response. This optimization was carried out to determine the optimum conditions for the triester yield in the transesterification of FPME with TMP. In this work, a set of 20 experiments were performed consisting of 8 core points, 6 star like points and 6 centre or null points. The distance of the star like point, α, used was 1.682. Precaution was taken to avoid systematic error by performing the experiments in random.

The optimization process result for the triester yield is given in Table 5. Design Expert 8.0.7.1 trial version was used to analyze the result. Temperature, reaction time and mole ratio of reactants were all fixed in the range of 140-160 °C, 4-6 hours and 4-6, respectively. It was found that within the given range, the highest triester yield of 81.42% was achieved at a temperature of 160 °C, reaction time of 6 h and FPME:TMP mole ratio of 6:1.

Table 5: Optimization result for TMP triester yield

Std	A = Temperature (°C)	B = Time (hours)	C = Mole Ratio	Actual Yield (%)	Predicted Yield (%)
1	140.00	4.00	4.00	51.23	50.35
2	160.00	4.00	4.00	54.16	54.34
3	140.00	6.00	4.00	70.73	70.94
4	160.00	6.00	4.00	79.58	81.15
5	140.00	4.00	6.00	67.51	66.39
6	160.00	4.00	6.00	69.88	70.12
7	140.00	6.00	6.00	72.54	72.81
8	160.00	6.00	6.00	81.42	82.75
9	133.18	5.00	5.00	64.51	65.64
10	166.82	5.00	5.00	79.12	77.36
11	150.00	3.32	5.00	49.21	50.37
12	150.00	6.68	5.00	80.11	78.32
13	150.00	5.00	3.32	64.66	64.23
14	150.00	5.00	6.68	79.27	79.06
15	150.00	5.00	5.00	78.01	78.37
16	150.00	5.00	5.00	79.01	78.37
17	150.00	5.00	5.00	77.89	78.37
18	150.00	5.00	5.00	78.05	78.37
19	150.00	5.00	5.00	77.91	78.37
20	150.00	5.00	5.00	79.23	78.37

ANOVA analysis for TMP triester yield

Design Expert 8.0.7.1 trial version was used to analyze the results. The summary of P-values and the model summary statistics are shown in Tables 6 and 7, respectively. A quadratic model was suggested from the CCD module with a high adjusted and predicted R-squared values of 0.9831 and 0.9381, respectively. The cubic model was aliased because the CCD does not contain enough runs to support a full cubic model. The analysis of variance (ANOVA) carried out confirmed the adequacy of the quadratic model.

Table 6: Summary of P-values for TMP triester yield

Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	Remark
Linear	0.0002	< 0.0001	0.6437	0.5452	
2FI	0.3816	< 0.0001	0.6507	0.3693	
Quadratic	< 0.0001	0.0169	0.9831	0.9381	Suggested
Cubic	0.0148	0.1577	0.9954	0.8859	Aliased

Table 7: Model Summary Statistics for TMP triester yield

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	Remark
Linear	6.07	0.6999	0.6437	0.5452	892.780	
2FI	6.01	0.7610	0.6507	0.3693	1238.16	
Quadratic	1.32	0.9911	0.9831	0.9381	121.60	Suggested
Cubic	0.69	0.9986	0.9954	0.8859	223.94	Aliased

Table 8: ANOVA analysis for TMP triester yield

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob>F
Model	1945.58	9	216.18	123.67	< 0.0001
A-Temperature	165.910	1	165.91	94.910	< 0.0001
B-Time	942.570	1	942.57	539.22	< 0.0001
C-Mole Ratio	265.550	1	265.55	151.91	< 0.0001
AB	19.3100	1	19.310	11.050	0.0077
AC	0.03500	1	0.0350	0.0200	0.8901
BC	100.470	1	100.47	57.470	< 0.0001
A^2	85.0100	1	85.010	48.630	< 0.0001
B^2	354.320	1	354.32	202.70	< 0.0001
C^2	81.3400	1	81.340	46.530	< 0.0001
Residual	17.4800	10	1.7500		
Lack of Fit	15.6600	5	3.1300	8.600	0.0169
Pure Error	1.82000	5	0.3600		
Cor Total	1963.06	19			

Std. Dev.	1.320		R-Squared	0.9911
Mean	71.70		Adj R-Squared	0.9831
C.V. %	1.840		Pred R-Squared	0.9381
PRESS	121.6		Adeq Precision	34.663

The ANOVA result is given in Table 8. All terms whose P-values are less than 0.05 are considered significant. Therefore, A, B, C, AB, BC, A^2, B^2 and C^2 are significant terms. The final equation in terms of coded factors was obtained as follows:

$$Y_{triester} = 78.37 + 3.49A + 8.31B + 4.41C + 1.55AB - 3.54BC - 2.43A^2 - 4.96B^2 - 2.38C^2 \quad (9)$$

The model F-value of 123.67 implies that the model is significant. The P-values were used as a tool to check the significance of each of the coefficients, which in turn are necessary to understand the pattern of the mutual interactions between the test variables (Shrivastava et al., 2008). The larger the magnitude of F-value and smaller the magnitude of P-value, the higher will be the significance of the corresponding coefficient (Borugadda & Goud, 2015; Alam et al., 2008).

The predicted R^2 value of 0.9381 agrees reasonably with the adjusted R^2 value of 0.9831. Adequate precision is a measure of the signal to noise ratio and it compares the range of the predicted value at the design points to the average prediction error. The adquate precision value greater than 4 is desirable for adequate model efficacy. Therefore, the obtained adequate precision value of 34.663 inidcates an adequate signal. Hence, this model can be used to navigate the design space. The fitness of the model equation was validated using the coefficient of regression, R^2. The high R^2 value of 0.9911 implies that 99.11% of the variability in the response can be explained by the model.

Normal plot of Residuals (Figure 6) and the Predicted vs Actual plots (Figure 7) were used to check the distribution of residuals. The close distribution of the points along the straight lines indicate a good relationship between the experimental values and the predicted values of the response. These plots also confirm that the chosen model was adequate for prediction of the response variables in the experimental values.

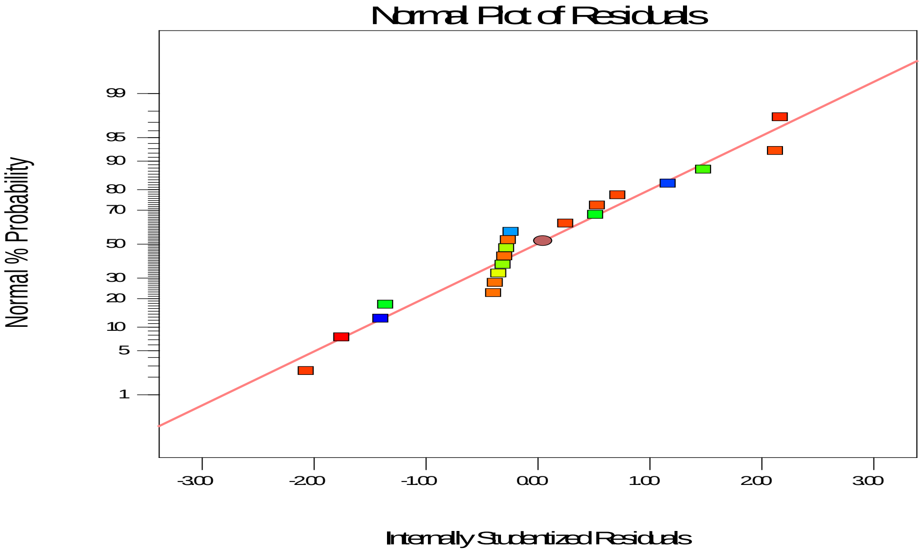


Fig. 6: Normal Plot of Residuals for TMP triester yield

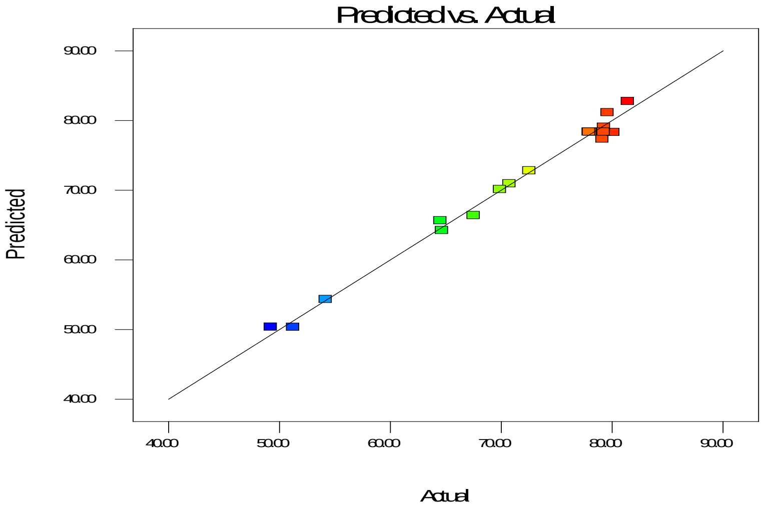


Fig. 7: Predicted Vs Actual plot for TMP triester yield

Response surface measurements

3D surface plots (Figures 8 to 10) were drawn to observe how triester yield varied as a function of any two factors selected for display. The nature of the response surface curves reveals the interaction between the variables. An elliptical shape in a curve depicts good interaction between the variables. The elliptical nature of the contour in the graphs indicates that there was a relative significant interaction between every two variables. It can also be observed from Figure 10 that a very strong interaction exists between molar ratio and time, and there was a maximum predicted triester yield as indicated by the surface confined in the smallest ellipse in the contour diagram.

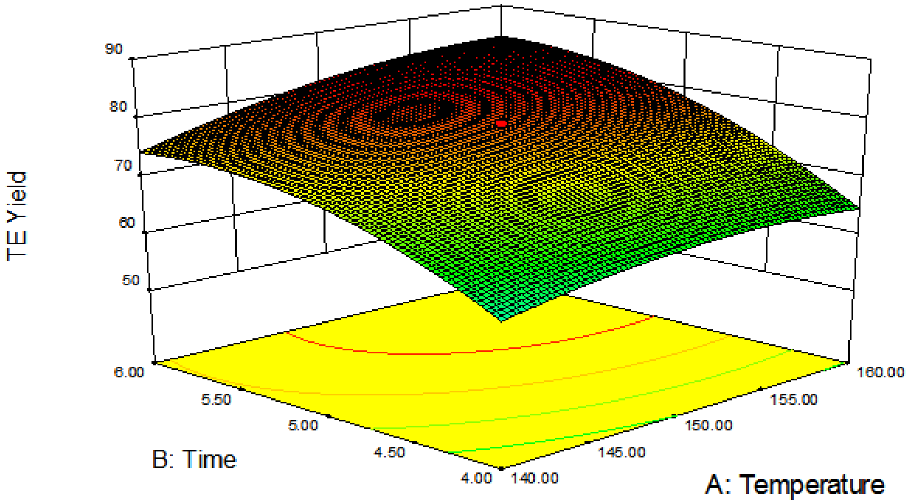


Fig 8: 3D Surface plot for triester yield showing combined effects of time and temperature

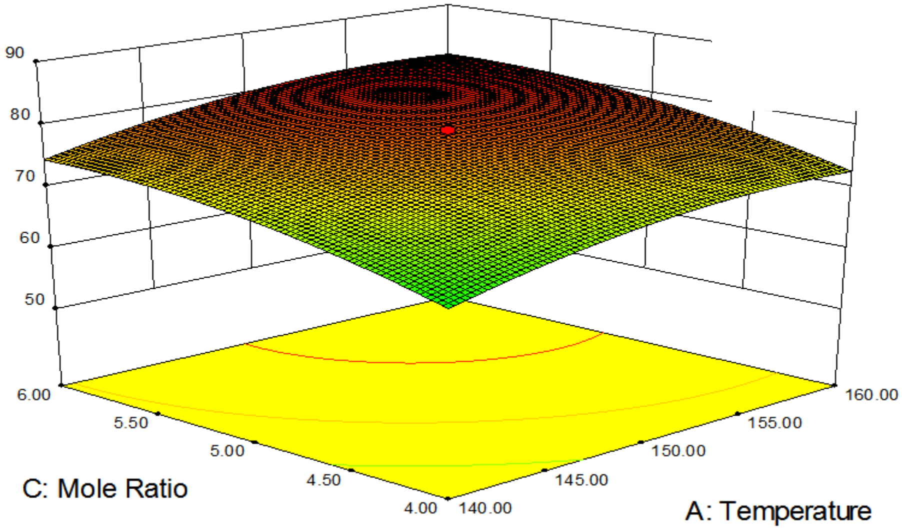


Fig 9: 3D Surface plot for triester yield showing combined effects of mole ratio and temperature

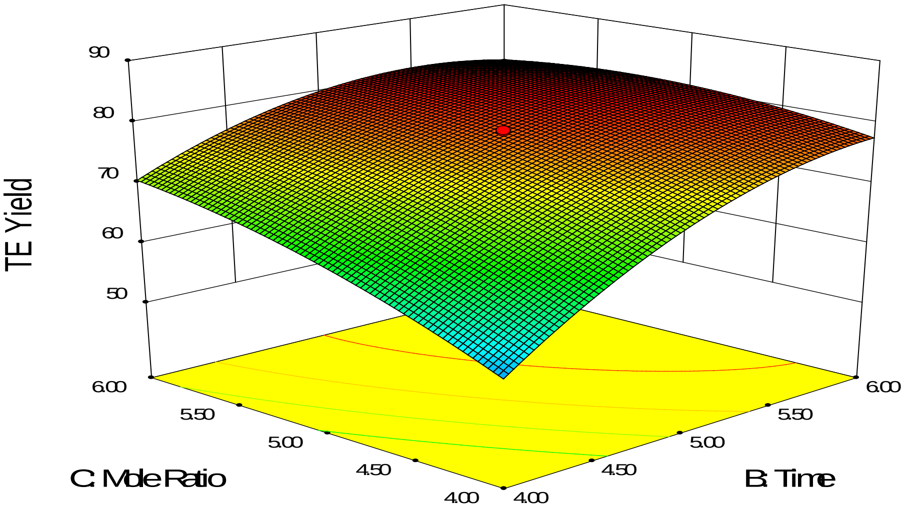


Fig 10: 3D Surface plot for triester yield showing combined effects of mole ratio and time

Validation of optimization result

The maximum triester yield at the developed optimum synthesis conditions as predicted by the model was 82.75%, while the actual maximum triester yield was 81.42%. Confirmatory experiment was conducted to verify the accuracy and applicability of the developed optimum conditions. The result of the replicate experiment is presented in Table 9. Triester yield of 81.98% was obtained. Hence, the optimum synthesis conditions developed were found to be valid for the experimental data. Thus, the optimum reaction conditions for maximum triester yield in the transesterification of FPME with TMP were temperature of 160 °C, reaction time of 6 hours and reactants mole-ratio of 6:1 at which triester yield was 81.42%.

Yunus et al. (2003) obtained 98% of palm oil TMP triester from palm oil methyl ester at the temperature of 130 °C, vacuum pressure of 20 mbar, catalyst (sodium methoxide) loading at 0.8% w/w and 3.9:1 mole-ratio by transesterification with TMP.

Table 9: Replicate experiments at optimum conditions

Parameters	Optimum conditions
Temperature (°C)	160
Time (hrs)	6.00
Mole Ratio	6:1
Actual triester yield (%)	81.42
Predicted triester yield (%)	82.75
Validated triester yield (%)	81.98

Analysis of lubrication properties

The lubrication properties of the synthesized FPBL were analyzed to determine its suitability for use as a biolubricant base fluid. The results are presented in Table 10 in comparison with the properties of raw FPSO, other biolubricants and the ISO (International Organization for Standardization) viscosity grades requirement. The kinematic viscosity, viscosity index, pour point and flash point of the samples were determined using American Society for Testing and Material (ASTM) standard methods D445, D2270, D97 and D92, respectively (ASTM 2003).

Table 1: Properties of FPBL in comparison with other plant based biolubricants and ISO grades

Properties	FPBL	FPSO	Calophyllum oil boilube[a]	Palm oil biolube[b]	ISO VG32[c]	ISO VG46[c]	ISO VG68[c]
Viscosity @ 40 °C (cSt)	60.78	55.75	56.40	52.40	> 28.80	> 41.40	> 61.40
Viscosity @ 100 °C (cSt)	11.03	10.30	8.80	10.20	> 4.10	> 4.10	> 4.10
Viscosity Index (VI)	176	176	193	186	> 90	> 90	> 198
Pour point (°C)	-14	-5	-3	-5	< -10	< -10	< -10
Flash point (°C)	220	152	218	-	-	-	-

[a]Taken from Widyawati et al. (2014).
[b]Taken from Yunus et al. (2003).
[c]Taken from Rudnick (2005).

Transesterification increased the kinematic viscosity of fluted pumpkin oil at 40 °C from 55.75 to 60.78 cSt and from 10.30 to 11.03 cSt at 100 °C, while the pour point and flash point of the oil were improved from -5 °C and 152 °C to -14 °C and 220 °C, respectively. High kinematic viscosity and viscosity index values are desirable for efficient performance of lubricants at high temperatures. Also, a high flash point is desirable for lubricants to avoid fire hazards at high temperatures. However, a low pour point value is required for efficient performance of lubricants in cold environments.

The lubrication properties of the synthesized FPBL were found comparable to those of other biolubricants. They equally met the requirement for ISO VG32 and VG46 grades. ISO VG46 grade lubricants are usually used for light gear applications, crankcase and as hydraulic fluids (Gunam Resul et al., 2012).

Conclusion

Biolubricant was successfully synthesized from FPME by chemical modification via transesterification process. The reaction followed a second order kinetic model with an overall rate constant of 2.05×10^{-1} (%wt/wt min ◦C)$^{-1}$ and a regression value of 0.958. The estimated activation energy for the synthesis of FPBL was 40.65 kJ/mol. Optimization of TMP triester yield using CCD gave the optimum conditions of 160 °C temperature, 6 h reaction time and FPME:TMP mole ratio of 6:1 for a triester yield of 81.42%. The lubrication properties of FPBL were found comparable to those of other plant based lubricants and equally met the requirement for ISO VG32 and VG 46 viscosity grades.

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Nomenclature

ANOVA	Analysis of variance
CCD	Central composite design
DE	Diester
E_a	Activation energy
FAME	Fatty acid methyl ester
FPBL	Fluted pumpkin biolubricant
FPME	Fluted pumpkin methyl ester
FPSO	Fluted pumpkin seed oil
K_{TMP}	Rate constant with respect to TMP
M	Methanol
ME	Monoester
NPG	Neopentyl glycol
PE	Pentaerythritol
POME	Palm oil methyl ester
PKO	Palm kernel oil
R	Gas rate constant
R^2	Correlation coefficient
RSM	Response surface methodology
RSO	Rubber seed oil
TAG	Triglyceride
t	Time
TE	Triester
TMP	Trimethylolpropane