Process Optimization and Modelling of Lubricant Base Stock Synthesis from Crude Palm Oil

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Abstract: **- In this study, crude palm oil was used as a precursor for the production of biolubricant base stock by a two-step transesterification process. Palm oil methyl ester produced from the first step was subsequently reacted with trimethylolpropane using calcium hydroxide as catalyst to produce palm based TMP ester. Optimization of lubricant base stock synthesis from palm oil methyl ester and trimethylolpropane was carried out using response surface methodology, central composite design (CCD). The optimum variable conditions were reaction temperature of 159.9^{o}C, mole ratio of 4.99, catalyst loading of 1.16 and reaction time of 211.63 minutes under vacuum pressure for 84.681% palm based TMP ester yield. Regression analysis of the data showed a second order quadratic regression model which establishes the link between variables and biolubricant yield with temperature and mole ratio being most significant variable. The coefficient of regression R^2 was 0.9477 implying that 94.77% of the irregularity in the response can be explained by the model. Lubricating properties of palm based TMP ester was evaluated and found to have the following lubricating properties: kinematic viscosity of 40.44 and 10.03 cSt at 40^{o}C and 100^{o}C respectively, viscosity index of 198, flash point of 187^{o}C and pour point of -6^{o}C. These properties of palm based TMP ester conforms to the standard specifications for ISO VG32 and VG46 viscosity grades, and were also found similar to other plant based biolubricants such as jatropha, sesame and canola biolubricant base stock and indicates good prospect as base stock in biodegradable lubricant formulation.**

Keywords: **Biolubricant, Crude palm oil, Response surface methodology Transesterification, Trimethylolpropane.**

I. INTRODUCTION

Petroleum based lubricants have been attributed with lot of negative impact on our environments owing majorly to its inherent properties of non-biodegrability, toxicity and non-renewability. This is evident from pollution, threats to occupational, human and aquatic safety caused by accidental discharge, total loss applications, refinery processes, etc. Also, the combustion of mineral oils as a lubricant has been proven to emit traces of metals, such as calcium, phosphorous, zinc, magnesium, and iron nanoparticles [11]. Moreover, the current and future prospects of mineral oils as lubricants in automobile engines was investigated and anticipated a declined future prospects was forecasted [7].These have rekindled researchers' interest on the search for a better alternative to petroleum based lubricants, one that will be easily renewable, non-toxic, biodegradable, ecofriendly and at the same time posses good lubricity property. Over the years, researchers has explored the prospects of biodegradable synthetic products, a renewable source as an alternative to petroleum based lubricants for industrial and transportation application just like bio-diesels[5]. Some works has also being carried out which confirmed the prospects of vegetable oils as an alternative fuels [24]. Bio- lubricants possess lower volatility, higher flash/ fire points, less vapor emissions and oil mist, and constant viscosity that make them offer better safety[15].

Vegetable oils are promising alternative to petroleum based base oil because of their good lubricity, non-toxic and biodegradable nature, low volatility and are also renewable. However, vegetable oils have some drawbacks which limit their application as lubricant base oil. Such properties include low thermal oxidative stability and high melting point [6]. Vegetable oil is made up of natural triglyceride (TAGs) consisting of glycerol back-bone and three esterified long chain fatty acids, the β hydrogen in glycerol is not suitable because of its instability and tendency to undergo elimination reaction which causes molecule degradation [10]. These drawbacks can be reduced by converting natural fatty acyl esters into synthetic esters using a more resistant polyol to replace the glycerol backbone [1, 4].

The chemical modification involves transesterification reaction whereby trimethylolpropane (TMP), a polyol is used to displace the glycerol backbone to yield synthetic ester [6]. This compound is also used to produce triesters (TE) compounds that can replace triacylgycerol in lubricants [1, 21] and produce vegetable oil based lubricants with improved properties. The major constituent of vegetable oil is triacylgycerol which is made up of carbon, hydrogen and oxygen that determines their characteristics. The general principle of synthesis of biolubricant from vegetable oil involves a two-step transesterification process, firstly, the base-transesterification reaction of triglyceride and alcohol to produce fatty acid acyl ester (FAAE) and subsequent reaction of FAAE and TMP to yield TMP ester. Previous studies reported over 85% yield of Fatty acid methyl ester (FAME) at 60^{o}C reaction temperature, 1% sodium hydroxide catalyst, methanol-to-oil molar ratio of 6.0 and 1 hour reaction time [8, 12, 20]. For the second step, the use of sodium methoxide to catalyze the reaction has been reported by many researchers [17, 18, 22].

Both edible and non-edible vegetable oils have been investigated for the synthesis of biolubricant. Palm kernel oil methyl ester has been successfully used to produce 98%

trimethylolpropane ester [23] while more than 80% biolubricant yield have been reported from jatropha oil [5, 26].75.0% yield of melon-based biolubricant successfully produced at the optimum mole ratio, time and temperature of 4:1, 5 hours, and 150^0C respectively [14] while jatropha curcas has also been reported as a feedstock for biolubricant production [3, 16]. The process variables that affects the conversion efficiency of the reaction has been reported to include temperature, catalyst loading, reaction time, molar ratio and pressure [13, 5, 3]. A mini pilot batch reactor was used for the process and obtained the following optimal conditions; temperature: 120°C, pressure: 20 mbar, molar ratio: 3.8: 1 (POME to TMP), 2 hours reaction time, catalyst: 0.9 w/w% and speed of agitation: 180 rpm [22].

Palm oil is speculated to be the world's top oil produced, although it is at the moment the second most produced after soybean oil [25].Palm oil has been speculated to be the most potential vegetable oil which can be used as raw material to produce biodiesel and also predicted an increased future potential for palm oil production [9]. Palm oil has an approximately equal percentage of saturated and unsaturated fatty acid giving it a distinctive characteristic. Its percentage composition in decreasing order is as follows; 44% C16:0; 39.2% C18:1; 10.1% C18:2; 4.5%C18:0; 1.1%C14:0; 0.4%C18:3; 0.2% C12:0.

The main objective of this study is to optimize the synthesis of lubricant base stock from crude palm oil using response surface methodology along with comparative study of the physiochemical properties of the obtained biolubricant with a known mineral base stock. Calcium hydroxide, a cheaper and readily available reagent was used to catalyze the second step transesterification reaction.

II. MATERIALS AND METHODS

2.1 Materials

Fresh crude palm oil was purchased from a local producer in Ihite-Afoukwu, Mbeise in Imo state, Nigeria. Trimethylolpropane (1, 1, 1-Tris (hydroxymethyl) propane dist., ≥ 98.0% (GC)) was purchased from Aldrich-Zigma, Germany. Calcium hydroxide, $Ca(OH)_2$ was purchased from Onitsha. Other reagents were of analytical grade ad also purchased from Onitsha.

2.2 Experimental procedure

The synthesis of palm oil TMP ester from crude palm oil (CPO) by a two step transesterification process is illustrated in Figure1

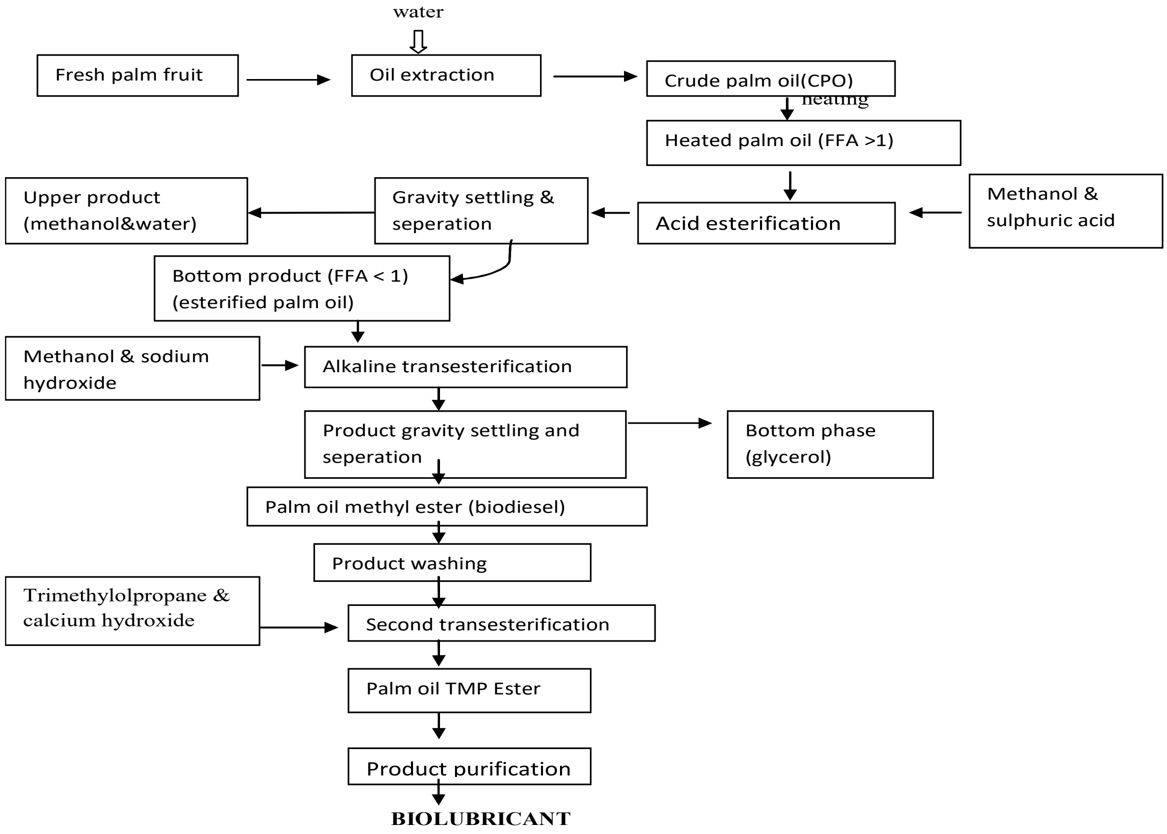
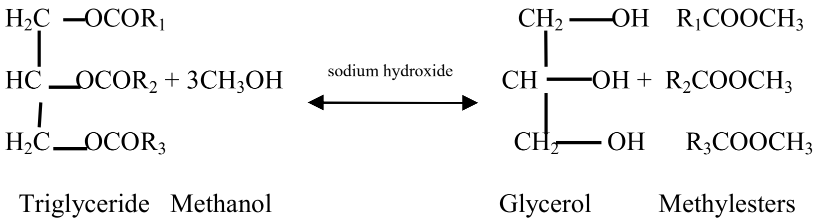


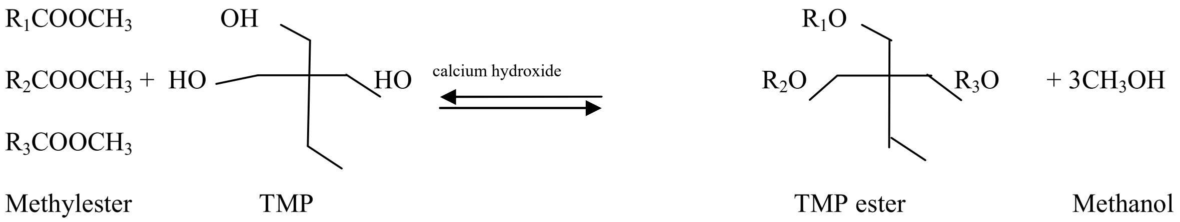
FIG. 1. Simplified flow diagram for the synthesis of palm oil TMP Ester

The percentage free fatty acid was first reduced to <1% by esterification reaction process, the esterified palm oil was converted to palm oil methyl ester (POME) and subsequently transesterified with TMP to produce palm based TMP ester, a biolubricant. The procedure for this reaction was carried out with modifications as described by [19] in batches. TMP was measured and added to the 500ml three-neck round bottom flask fitted with a water-cooled reflux condenser, a thermometer and a magnetic stirrer. The substance was heated to 110^{o}C with constant stirring under CO_2 line using kipp's apparatus until it melted. The heating continued at that temperature for another 15 miuntes to allow moisture form due to the hygroscopic nature of TMP to dry. Then, a known quantity of POME was introduced into the reactor with respect to the molar ratio of POME: TMP and heated to the specified temperature. The catalyst was then added and left to react over a specific period of time. The mixture was allowed to cool after the time elapsed using an ice bath and the catalyst filtered out. The percentage composition of the product mixture was analyzed by Gas chromatography analysis (GC) while FTIR was used to determine the funtional group in the product mixture.Also, the lubricating properties of palm based TMP ester were evaluated according to ASTM standard [2]. The reaction equation is illustrated in Equ. 1.

First step



Second step



2.3 Design of Experiment for palm based TMP ester synthesis

Design Expert Software Version 11 central composite design (CCD) was used to design and array 30 experimental runs to study the effect of process variables on response and also the interactive effect of the process variables. The runs where taken randomly to avoid systematic error. The study also embodied a response surface analysis, regression analysis and ANOVA analysis. Table 1 shows the process variables range for the design.

Table 1 Factors levels of independent variable for palm based TMP ester synthesis

Independent variables	Units	Low Level	High Level	-alpha	+alpha
Temp	deg.C	100	160	70	190
molar ratio		2	5	0.5	6.5
catalyst loading	%wt	0.6	1.2	0.3	1.5
Time	mins	90	240	15	315

III. RESULTS

3.1 Design Matrix and Response using Central Composite Design

The process design matrix and responses was shown in Table 2. It shows the combined effects of four important independent variables: temperature, mole ratio, catalyst loading and time on palm based TMP ester (response). The highest percentage yield of palm based TMP ester was 84.26% at 160^{o}C, catalyst loading of 1.2% wt/wt, mole ratio of 5 and time of 240mins. Design Expert 11.0 trail version was used to analyze the result.

Table 2 Design Matrix and Response for Palm based TMP ester

Std	Run	Factor 1 Temperature (deg.C)	Factor 2 POME:TMP	Factor 3 Catalyst loading (%wt/wt)	Factor 4 Time (mins)	Actual Response Yield%	Predicted Response Yield %
1	23	100	2	0.6	90	68.34	68.56
2	18	160	2	0.6	90	71.46	70.35
3	3	100	5	0.6	90	73.05	71.99
4	10	160	5	0.6	90	75.17	76.23
5	28	100	2	1.2	90	70.82	70.32
6	15	160	2	1.2	90	73.91	72.95
7	13	100	5	1.2	90	75.01	74.65
8	8	160	5	1.2	90	80.12	79.73
9	27	100	2	0.6	240	70.78	70.20
10	1	160	2	0.6	240	73.15	73.70
11	14	100	5	0.6	240	75.02	76.17
12	20	160	5	0.6	240	82.59	82.12
13	25	100	2	1.2	240	71.43	70.55
14	30	160	2	1.2	240	74.81	74.89
15	17	100	5	1.2	240	77.3	77.43
16	11	160	5	1.2	240	84.26	84.22
17	4	70	3.5	0.9	165	72.82	73.82
18	26	190	3.5	0.9	165	79.31	79.88
19	6	130	0.5	0.9	165	70.88	72.80
20	2	130	6.5	0.9	165	82.18	81.83
21	21	130	3.5	0.3	165	72.4	72.24
22	24	130	3.5	1.5	165	73.24	74.97
23	5	130	3.5	0.9	15	64.76	66.62
24	22	130	3.5	0.9	315	71.24	70.95
25	9	130	3.5	0.9	165	73.45	73.65
26	7	130	3.5	0.9	165	75.26	73.65
27	16	130	3.5	0.9	165	74.66	73.65
28	12	130	3.5	0.9	165	72.86	73.65
29	19	130	3.5	0.9	165	73.6	73.65
30	29	130	3.5	0.9	165	75.19	73.65

3.2 ANOVA analysis for Palm based TMP ester yield

The model summary test and the lack of fit test for the palm based TMP ester yield was presented in Tables 3 and 4 respectively. The highest order polynomial where the additional terms are significant and the model is not aliased was selected. The summary of P-values indicates that a quadratic model fitted the ANOVA analysis and hence it was suggested. The linear and 2FI models were not suggested while the cubic model was aliased because the CCD does not contain enough runs to support a full cubic model. A significance level of 95% was used hence all the terms whose P-value are less than 0.05 are considered significant.

Table 3 Summary of P-values for Palm based TMP ester

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	0.0211	0.6717	0.6034	Not suggested
2FI	0.8124	0.0140	0.6253	0.5549	Not suggested
Quadratic	< 0.0001	0.2108	0.8989	0.7673	Suggested
Cubic	0.6074	0.0838	0.8885	-1.1951	Aliased

Table 4 Lack of Fit Tests for palm based TMP ester

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Linear	137.46	20	6.87	6.83	0.0211	
2FI	118.58	14	8.47	8.42	0.0140	
Quadratic	21.30	10	2.13	2.12	0.2108	Suggested
Cubic	8.53	2	4.26	4.24	0.0838	Aliased
Pure Error	5.03	5	1.01			

Table 5 shows the ANOVA for triester quadratic model, P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, A^2, B^2, D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The final quadratic model equations obtained for the yield of palm based TMP ester (triester) in terms of coded factors are

$$\text{Triester } (\%) = +73.65 + 2.14*A + 3.19*B + 0.9644*C + 1.53*D + 1.60*A^2 + 1.83*B^2 - 2.43*D^2$$

From the model equation, the co-efficient of molar ratio is the highest positive value thus is the most significant variable in the conversion. Positive coefficient of model term implies that an increase in the variable will result to a gain in yield.

Table 5 ANOVA for Quadratic model Response (triester)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	477.19	14	34.09	19.42	< 0.0001	Significant
A-temp	92.01	1	92.01	52.42	< 0.0001	
B-molar ratio	203.53	1	203.53	115.96	< 0.0001	
C-catalyst loading	18.60	1	18.60	10.60	0.0053	
D-time	46.89	1	46.89	26.72	0.0001	
AB	6.00	1	6.00	3.42	0.0842	
AC	0.7056	1	0.7056	0.4020	0.5356	
AD	2.92	1	2.92	1.67	0.2163	
BC	0.8190	1	0.8190	0.4666	0.5050	
BD	6.48	1	6.48	3.69	0.0739	
CD	1.95	1	1.95	1.11	0.3090	
A^2	23.94	1	23.94	13.64	0.0022	
B^2	31.39	1	31.39	17.88	0.0007	
C^2	0.0041	1	0.0041	0.0024	0.9619	
D^2	55.16	1	55.16	31.43	< 0.0001	
Residual	26.33	15	1.76			
Lack of Fit	21.30	10	2.13	2.12	0.2108	not significant
Pure Error	5.03	5	1.01			
Cor Total	503.52	29				

Table 6 Fit Statistics

Std. Dev.	1.32		R^2	0.9477
Mean	74.30		Adjusted R^2	0.8989
C.V. %	1.78		Predicted R^2	0.7673
			Adeq Precision	18.7929

Figure 2 and 3 shows the normal plot of Residuals and Predicted vs Actual plot respectively. From the plots, it can be seen that the points were closely distributed along the straight line of the plot in the figures, it confirms the good relationship between the experimental values and the predicted values of the response though some small scatter like an 'S' shape is always expected. These plots equally confirm that the selected model was adequate in predicting the response variable in the experimental values.

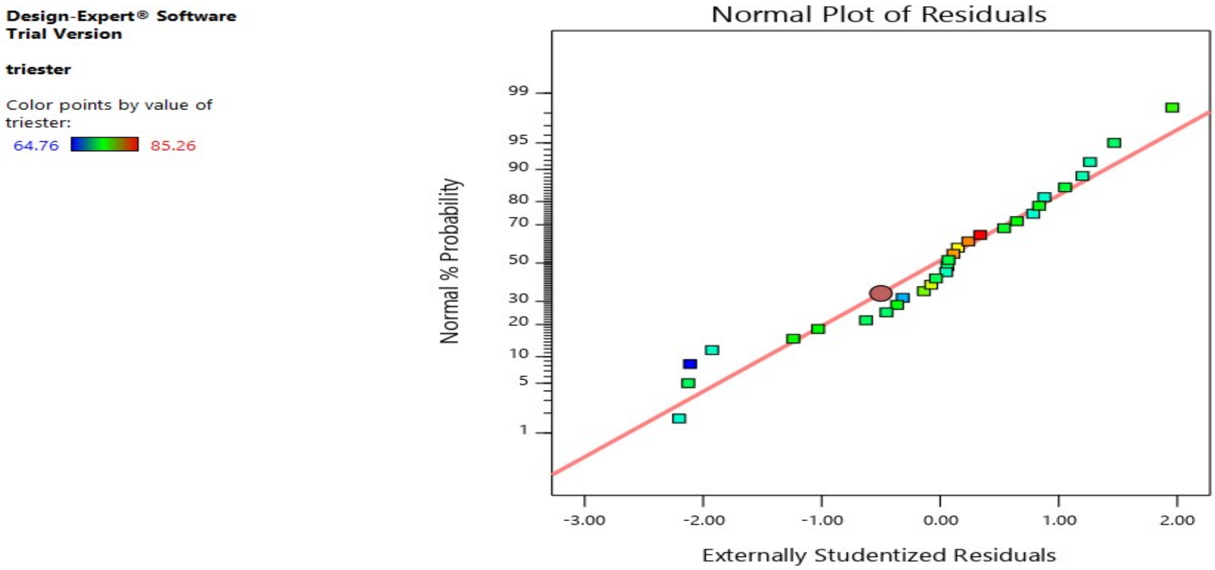


Fig 2: Normal plot of Residual for palm based TMP ester

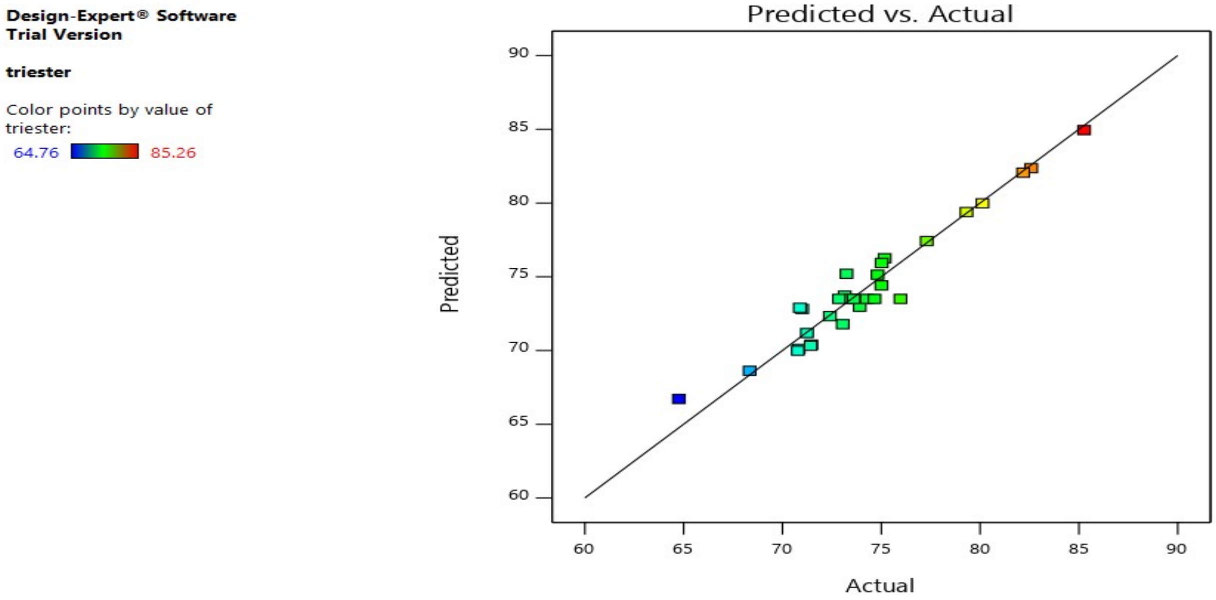


Fig 3: Predicted vs Actual plot for palm based TMP ester

3.3 2D Response Surface Studies

Two factor-at-a-time response surface plots were drawn for the four reaction parameters of reaction temperature, mole ratio, catalyst loading and time. The triester (TE) yield was found to vary between 68.34 and 84.26 wt%. Figure 4 shows plots for the effects of temperature and mole ratio on TE yield, the time and catalyst loading was fixed at 240mins and 1.2 wt% respectively. Figure 5 shows plot for the effect of temperature and catalyst loading on TE yield, the time and mole ratio was fixed at 240 minutes and 5 respectively.

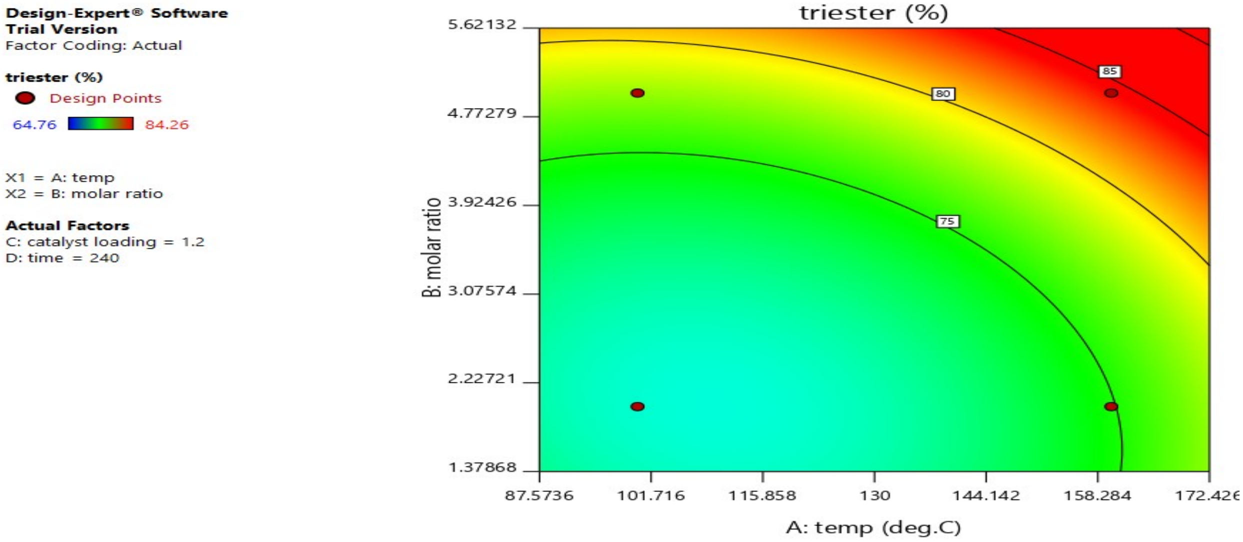


Fig 4: 2D Surface plot for effect of temperature and mole ratio on TE yield obtained from transesterification reaction of TMP with POME at a catalyst loading of 1.2 wt% and 240mins.

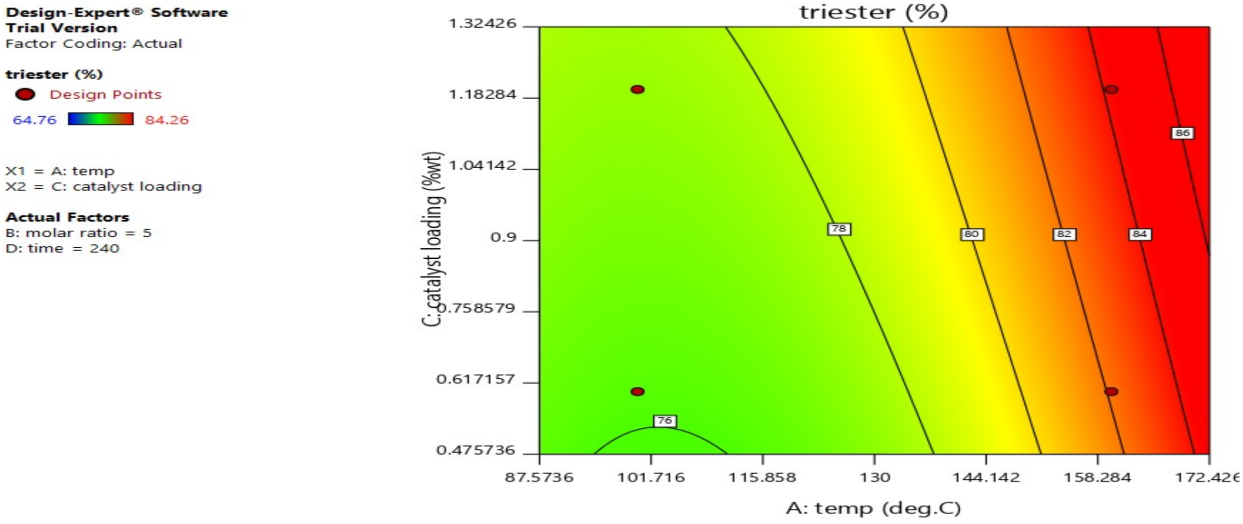


Figure 5: 2D surface plot for effect of temperature and catalyst loading on TE yield obtained from transesterification reaction of TMP with POME at mole ratio of 5 and 240mins.

3.4 3D Response Surface and Contour Plot

The response surface shows the interactive effect of process variables on the response, the response surface contours which are graphical results of interactive effects are shown in Figure 6 – 10. The optimum value of Y was 84.26%. The response surface of extent of conversion showed a clear peak, indicating that the optimum condition for maximum yield was well within the design perimeter. It could be observed from the 3D plot the conversion increased when mole ratio and temperature increased. It was observed that temperature and mole ratio increased the yield in a parabolic pattern. Figure 6 shows a very strong interaction of temperature and molar ratio at fixed catalyst loading and temperature. It was observed that the conversion increased steadily with a corresponding increment in temperature and molar ratio.

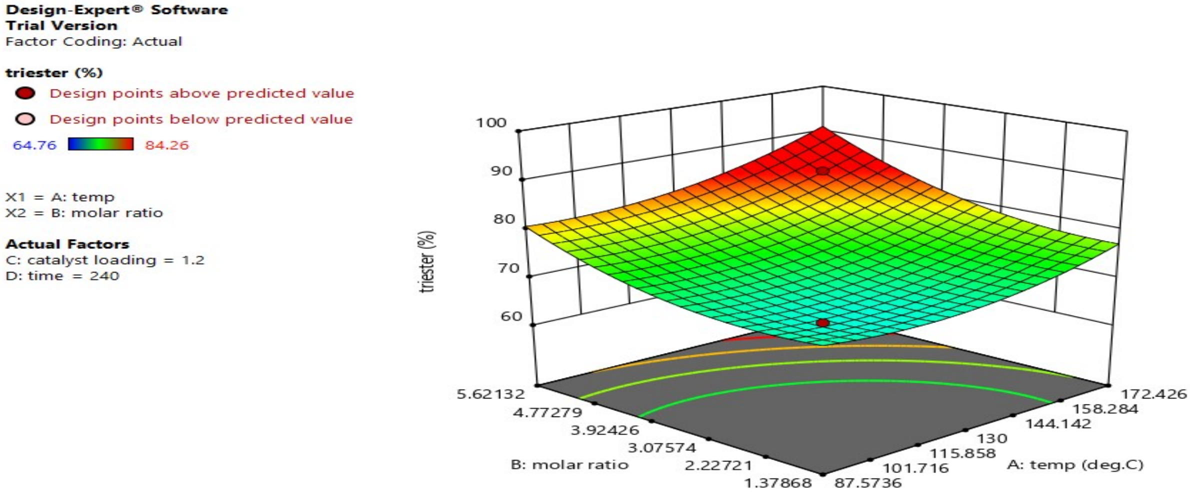


Fig 6: 3D contour plot for effect of temperature and POME -to-TMP molar-ratio on TE

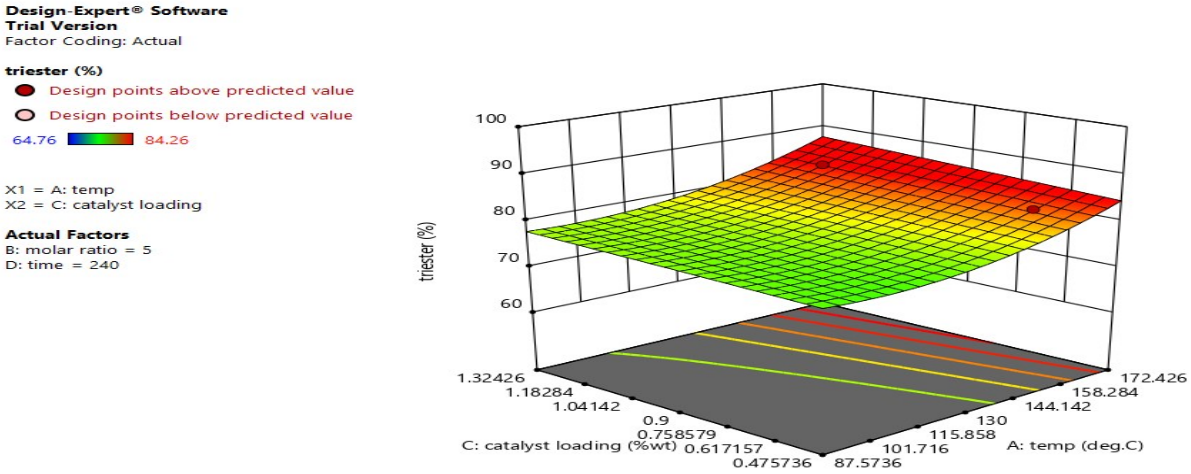


Fig 7: 3D contour plot for effect of temperature and catalyst loading on TE yield

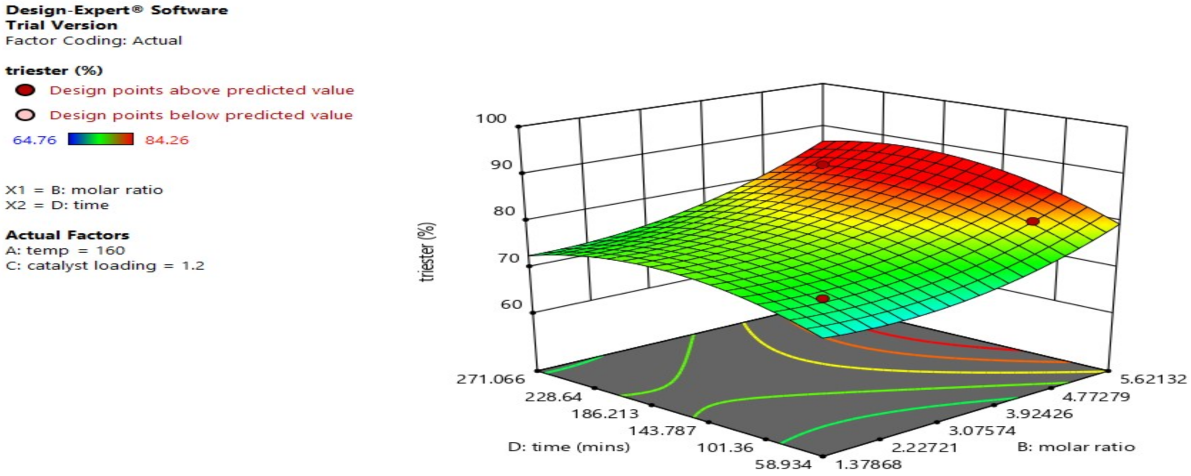


Fig 8: 3D contour plot for effect of POME -to-TMP molar-ratio and time on TE yield

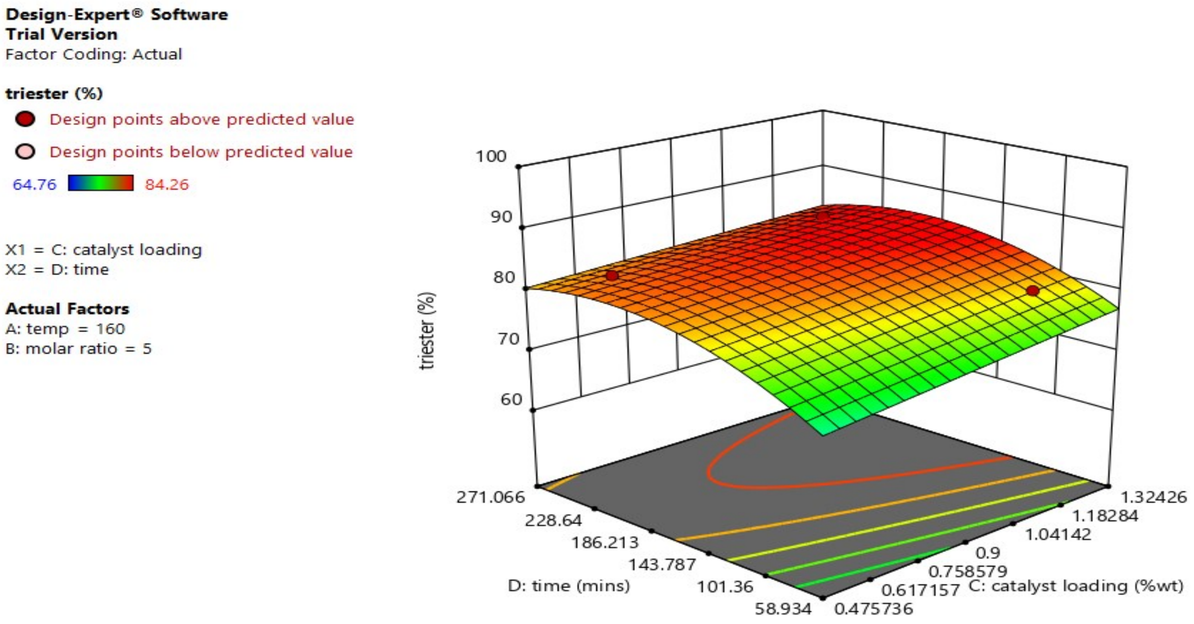


Fig 9: 3D contour plot for effect of catalyst loading and time on TE yield

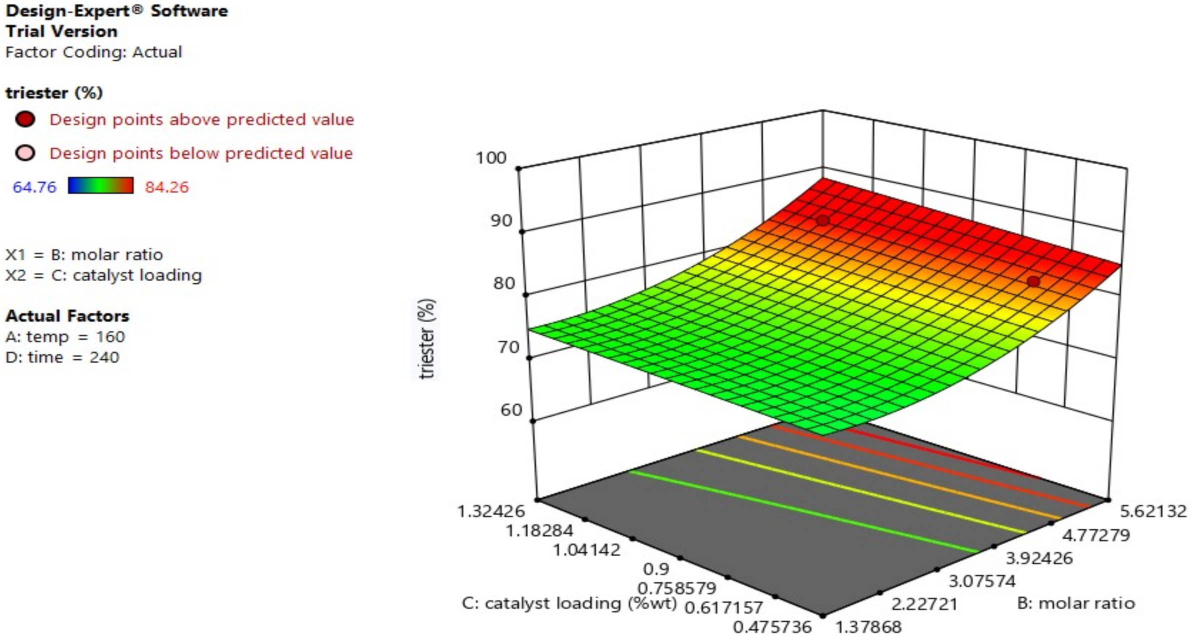


Fig 10: 3D contour plot for effect of catalyst loading and mole ratio on TE yield.

3.4 Optimization studies

Design expert version 11.0 was also used to optimize the process yield to achieve the maximum yield of TE. Predicted responses were generated using point prediction node (under optimization node in the CCD module). The best solution for the yield of 84.681% palm based TMP ester at reaction temperature of 159.9^{o}C, mole ratio of 4.99, catalyst loading of 1.16 and reaction time of 211.63 minutes under vacuum pressure as shown in Figure 11

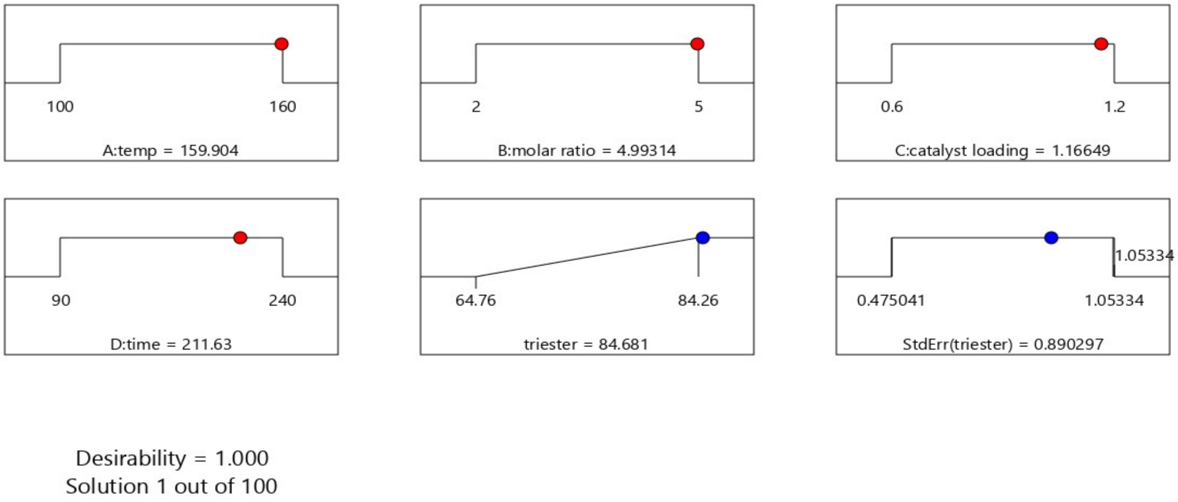


Fig 11: solution to numerical optimization of TE yield in CCD module for the transesterification of TMP and POME

3.5 Validation of optimization result

Six experiments were performed to check for reproducibility of data using the optimum conditions obtained from the optimization studies. The result shows that the palm based TMP ester yield varied between 84.1 - 85.5 wt percent. Figure 12 shows a plot of the six experiments at the optimum conditions. It was observed that the replicates showed excellent similarities in product development. It was seen that these yields differed by less than 2.0 wt %, while the standard deviation between these values was found to be less than 0.75%. Thus, it is confirmed that the transesterification experiments were repeatable and reproducible.

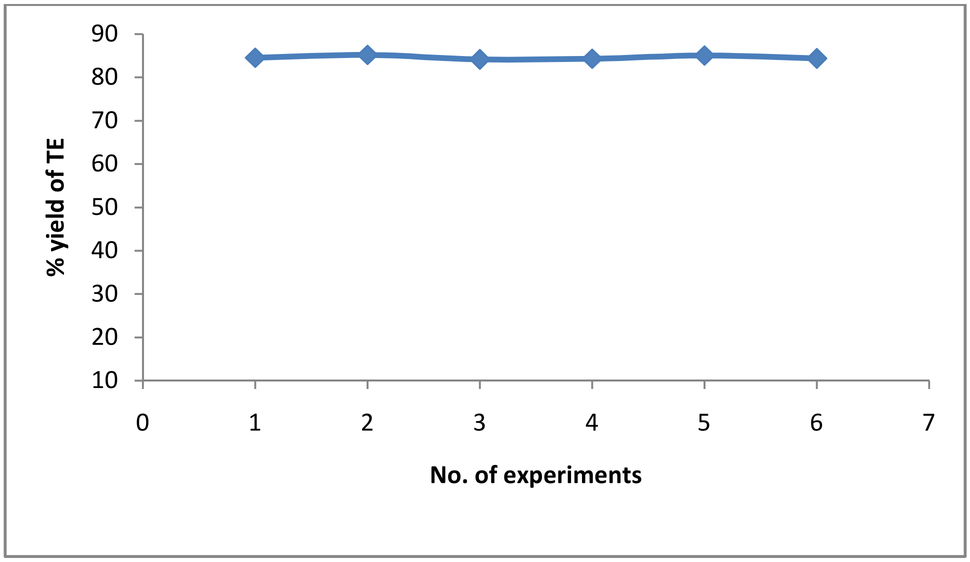


FIG.12. Reproducibility plot of six experiments for the transesterification of TMP and POME at the optimum condition.

3.6 Qualitative analysis of palm based TMP ester

The lubricating properties of palm based TMP ester was investigated using procedures from ASTM. Table 7 shows the qualitative analysis of palm based TMP ester as derived from this work compared to other vegetable based biolubricant reported by other authors. The viscosity of the palm based biolubricant base stock met ISO VG 46 and VG 22 specification for industrial grade light gear oil and was also found to exhibit high viscosity index (>190).

Table 7 Properties of Palm oil based biolubricant and comparison with other plant based biolubricant

Property	Viscosity @ 40ºC (cSt)	Viscosity@ 100ºC (cSt)	Viscosity index (VI)	Pour point (PP) (ºC)	Flash point (FP) (ºC)	Reference
This work	49.44	10.03	198	-6	187	
Palm kernel oil	52.4	10.2	186	-5		Yunus *et al*. (2003)
Jatropha Based Lube	42.37	9.37	183	-3	-	Muhammed *et al*. (2011)
Sesame Based Lube	35.55	7.66	193	-21	196	Ocholi *et al*. (2017
Castor oil Based lube	45.3	9.21	191	-8	215	Musa et al. (2015)

IV. CONCLUSION

Palm based TMP ester was successfully synthesized from crude palm oil through transesterification processes. The optimum synthesis conditions developed by the CCD model for prediction of TE yield were reaction temperature of 160ºC, mole ratio of 5, catalyst loading of 1.17 and reaction time of 212 minutes. The predicted TE yield at these conditions was 84.68 wt%. The palm based biolubricant base stock obtained conforms to the standard requirements for ISO VG 46 and VG 22 specification for industrial grade light gear oil, it was also found that the palm based TMP ester exhibit high viscosity index (>190) thus will show smallchange in viscosity with temperature change.

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