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Research Article

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The synthesis and optimization of a trimethylolpropane based biolubricant from a lard oil base stock

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Abstract A lard oil based biolubricant was synthesized through a two stage transesterification reaction. Raw lard oil was synthesized with methanol using potassium hydroxide as catalyst to produce a methyl ester for the first stage transesterification while the second stage involved the synthesis of the methyl ester and trimethylolpropane with sodium methoxide as catalyst to produce the lard oil based TMP ester. The optimization of the lard oil based TMP ester was carried out using a central composite design (CCD) of response surface methodology. The optimal conditions for the various independent variables were reaction temperature of 130 ºC, mole ratio of 1:4, catalyst weight of 1.5%w/w and reaction time of 180mins for a corresponding lard oil based TMP ester yield of 93%. Analysis of variance (ANOVA) of the response showed a quadratic regression model with interacting independent variables. Regression coefficient (R^2) of 0.972 and a standard deviation of 0.631 implies that 97.2% of the changes in the response can be explained by the regression model. The lubricating properties of the lard oil biolubricant are as follows: pour point of -10ºC, flash point of 229ºC, viscosity index of 2.32, specific gravity of 0.92g/ml and kinematic viscosity of 40.51 and 10.22cSt at 40 ºC and 100 ºC respectively. This study showed that the properties of the lard oil based TMP ester meets the ISO VG32 grade requirement and has its potential as a base oil for gear oil in automobiles.

Keywords Biolubricant, transesterification, raw lard oil, trimethylolpropane, central composite design

1. Introduction

The use of fossil fuel is a big global problem as it poses a great environmental threat. These fuels are connected to the release of greenhouse gases which are the leading cause of climate change, flooding, drought, and the spread of infectious diseases [2]. The reduction in crude oil reserves, poor biodegradability of mineral oils and increase in price of crude oil have established the need for bio-based fuels and lubricants. Fossil fuels like raw coal, methane gas and gasoline have been linked to being the major cause of global warming [4]. The reserves of non-renewable energy source are in danger of being exhausted in the foreseeable future [3]. Plant and animal oils are useful alternatives to mineral oils due to their good chemical properties such as biodegradability, high viscosity index and high flash point [1]. On the other hand, there poor thermal oxidative stability, high melting point and low temperature flow properties are major setbacks in their usage as a biolube base oil. This study is centered on the synthesis of raw lard oil with trimethylolpropane to produce a TMP based ester (biolubricant) which is an excellent alternative to mineral based lubricants. The lard oil which is a triglyceride consists of three fatty acids attached to a glycerol backbone, the beta hydrogen in the glycerol is the weak link in the triglyceride due to its tendency to undergo elimination reaction which leads to the rancidity and poor temperature flow properties of the lard oil [5].

There is a great interest in the agricultural sector in many countries of the world. Many entrepreneurs are venturing into various agricultural sectors. One area where there has been keen interest is pig farming. Pigs are known to have high birth rate and very low mortality rate of any livestock. The fats from pigs have been known to be used in different applications except in the synthesis of a bio-based biolubricant. The major composition of the fatty acid of lard oil are as follows: stearic acid (10-20%), palmitic acid (21-25%), oleic acid (41-44%) and linoleic acid (10-20%) [7,8]. The objective of this research work is the chemical modification of the triglyceride of the raw lard oil through the application of a two stage transesterification process. The reaction mechanism involves the synthesis of the lard oil with methanol to form a methyl ester which is an intermediate product of the first stage transesterification reaction and the further synthesis of the methylester with trimethylolpropane to form a TMP based ester(biolubricant) for the second stage transesterification reaction [6]. The catalyst being used for both the first and second stage transesterification reaction are potassium hydroxide and sodium methaoxide respectively. The process variables that are studied in this work includes the reaction time, temperature, catalyst weight and mole ratio. The optimization of this process variables to give an optimal biolubricant yield was carried out using the central composite design (CCD) of the response surface methodology (RSM).

2. Materials and Methods

2.1. Materials

Raw pig fats samples were collected from Onitsha main market, Anambra state Nigeria while the reagents and chemicals used in this research work were sourced from Eddyson International and chemical stores, Anambra, Nigeria.

2.2. Methods

2.2.1. Rendering of raw pig fat sample

Lard oil was extracted from the raw pig fat sample through the rendering process. The raw pig fat was sliced into smaller pieces before being placed into a clean beaker to be heated on a hot plate for thirty minutes. After heating, a notable mixture of lard oil and some cracklings were obtained. The extracted lard oil was separated from the cracklings through sieving with a cloth-like material. The extracted lard oil was poured into a jar and properly corked while the cracklings were disposed.

2.2.2. First stage transesterification reaction

100ml of raw lard oil underwent transesterification process with concentrated methanol using potassium hydroxide as catalyst to produce a methyl ester (biodiesel) in a continuously stirred reactor. The weight ratio of the lard oil to methanol was 1:6, the amount of catalyst used was 0.5%w/w of the weight of the lard oil at a reaction temperature and time of 60 ºC and 2h respectively [9].

2.2.3. Second stage transesterification reaction

In this process, the methyl ester (biodiesel) underwent a transesterification reaction with trimethylolpropane with sodium methoxide as catalyst to produce a biolubricant. This reaction was executed in a three necked round bottom flask connected to a reflux condenser and a mechanical stirrer. The weight ratio of the methyl ester to trimethylolpropane was 4:1, the amount of catalyst used was 0.8%w/w of the total weight of the reactants at a reaction temperature and time of 150 ºC and 3h respectively. The reaction was performed under vacuum condition to promote a forward reaction for high biolubricant yield as well as the total removal of methanol by-product [9].

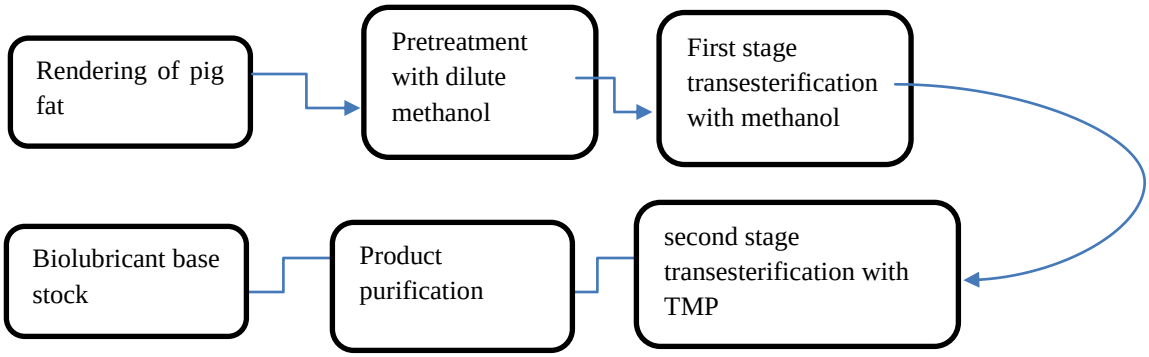
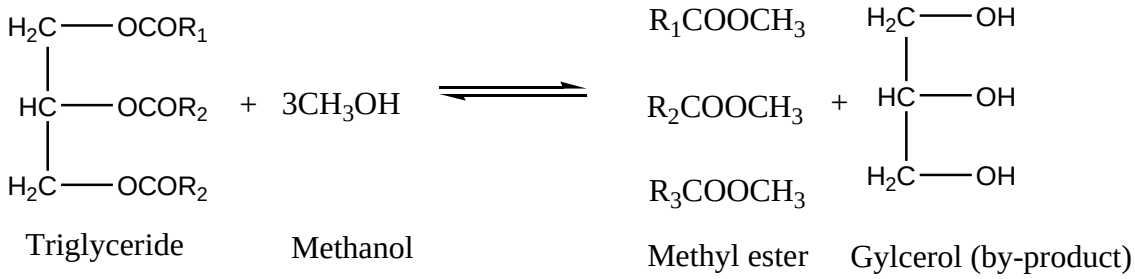
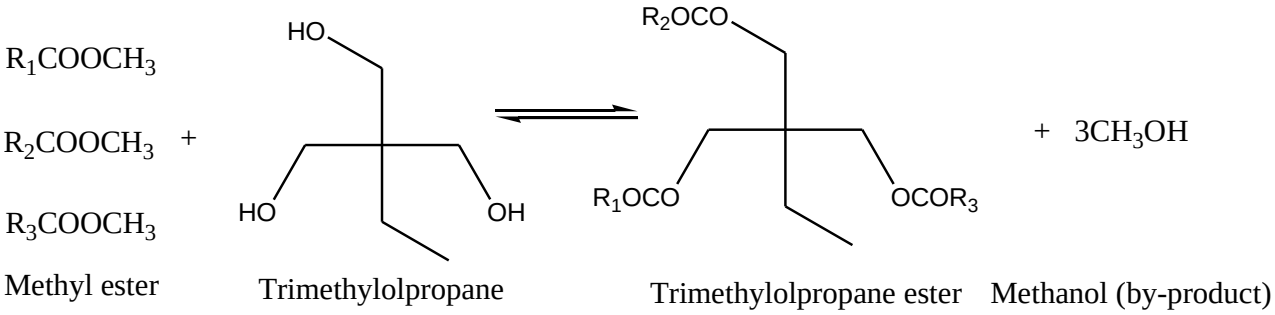


Figure 1: Flow diagram for the biolubricant synthesis of lard oil basestock

First stage



Second stage



2.3. Design of Experiment of Lard oil based biolubricant

Design Expert software (version 13) was used in this study to design the experiment and optimize the reaction conditions. The experimental design used in this study was the central composite design for the biolubricant synthesis. The responses measured which is the dependent variable is the percentage yield of the biolubricant. To optimize the process variables for biolubricant production, the central composite package will carryout an examination of the combined effects of the four different independent variables; reaction temperature, catalyst amount, TMP to oil ratio, reaction time and derive a model, taking into account, five levels and four factors factorial design which includes 2^4 = 16 factorial points plus 6 central points and 2×4 = 8 star points leading to a total of 30 experiments. The matrix for the four variables will be derived at three levels (-α, -1, 0, +1, +α). As normal, the experiments will be performed in random order to avoid systematic error. The regression analysis will be performed to estimate the response function as a second order polynomial.

Table 1: Independent variable factors for Lard oil TMP ester

Independent variables	Units	-alpha	Low level	Mid level	High level	+alpha
Temperature	^{o}C	120	130	140	150	160
Molar ratio	-	2.5:1	3:1	3.5:1	4:1	4.5:1
Catalyst	%wt	0.75	1	1.25	1.5	1.75
Time	Mins	160	180	200	220	240

3. Results & Discussion

3.1. Design matrix and response of Lard oil based TMP ester using central composite design

The combined effects of the four independent variables: reaction time, catalyst weight, temperature and mole ratio for the optimal yield of Lard oil based TMP ester can be seen in Table 2.0. The maximum yield of the TMP ester was 93% which was achieved at a temperature of 130^{0}C, catalyst weight of 1.5%w/w, molar ratio of 4:1 and reaction time of 150mins Robiah et al. [10], recorded a maximum yield of 98% for a palm oil based TMP ester, which is significantly higher than what was achieved for the lard oil based TMP ester but had the same optimal temperature of 130^{0}C. Similar works by Mohammed et al. [11] on the synthesis of palm kernel based TMP ester obtained a yield of 93.08% which is close agreement with what was gotten in this work but had a slight deviation in his reaction temperature of 135^{0}C and reaction time of 2.48h (150mins).

Table 2: Design Matrix and Response for Lard oil based TMP ester

		Factor 1	Factor 2	Factor 3	Factor 4	Actual Response
Std	**Run**	**X_1: Mole ratio (-)**	**X_2: Temperature (^{0}C)**	**X_3: Reaction time (mins)**	**X_4: Catalyst weight (w/w)**	**Yield (%)**
1	1	3	130	180	1	80.20
2	17	4	130	180	1	88.60
3	11	3	150	180	1	82.39
4	29	4	150	180	1	86.90
5	20	3	130	220	1	87.45
6	8	4	130	220	1	86.25
7	16	3	150	220	1	89.17
8	10	4	150	220	1	85.67
9	2	3	130	180	1.5	85.83
10	4	4	130	180	1.5	93.00
11	22	3	150	180	1.5	83.56
12	19	4	150	180	1.5	85.96
13	24	3	130	220	1.5	88.66
14	5	4	130	220	1.5	85.30
15	23	3	150	220	1.5	86.71
16	6	4	150	220	1.5	80.10
17	26	2.5	140	200	1.25	84.83
18	15	4.5	140	200	1.25	87.00
19	9	3.5	120	200	1.25	87.59
20	7	3.5	160	200	1.25	84.70
21	30	3.5	140	160	1.25	85.19
22	3	3.5	140	240	1.25	87.79
23	25	3.5	140	200	0.75	84.44
24	14	3.5	140	200	1.75	87.13
25	13	3.5	140	200	1.25	88.60
26	21	3.5	140	200	1.25	89.50
27	18	3.5	140	200	1.25	88.30
28	27	3.5	140	200	1.25	88.00
29	12	3.5	140	200	1.25	87.80
30	28	3.5	140	200	1.25	88.80

3.2. ANOVA analysis for Lard oil based TMP ester

The P-values showed that the quadratic model fitted the ANOVA while that of the cubic model is aliased because of CCD inability to incorporate all experimental runs to support a full cubic model. The 95% significant level was applied to this model invariably ensuring that all terms whose P-values are less than 0.05 are considered significant. From table 3 the larger model F-value of 36.64 implies that the model is also significant and is validated by the smaller P-value of 0.0001.

Table 3: ANOVA for Quadratic model Response of the Lard oil based TMP ester

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	204.07	14	14.58	36.64	< 0.0001	Significant
X_1-Mole ratio	6.15	1	6.15	15.46	0.0013	
X_2-Temperature	17.70	1	17.70	44.49	< 0.0001	
X_3-Reaction time	2.71	1	2.71	6.82	0.0196	
X_4-Catalyst weight	2.58	1	2.58	6.49	0.0223	
X_1X_2	12.62	1	12.62	31.73	< 0.0001	
X_1X_3	86.26	1	86.26	216.85	< 0.0001	
X_1X_4	4.63	1	4.63	11.65	0.0039	
X_2X_3	0.4935	1	0.4935	1.24	0.2829	
X_2X_4	20.45	1	20.45	51.42	< 0.0001	
X_3X_4	20.32	1	20.32	51.08	< 0.0001	
X_1^2	12.05	1	12.05	30.29	< 0.0001	
X_2^2	10.05	1	10.05	25.26	0.0002	
X_3^2	7.39	1	7.39	18.58	0.0006	
X_4^2	13.26	1	13.26	33.34	< 0.0001	
Residual	5.97	15	0.3978			
Lack of Fit	4.09	10	0.4087	1.09	0.4937	Not significant
Pure Error	1.88	5	0.3760			
Cor Total	210.04	29				

Table 4: Model Summary Statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	2.69	0.1388	0.0010	-0.2858	270.07	
2FI	1.38	0.8280	0.7375	0.6658	70.19	
Quadratic	0.6307	0.9716	0.9451	0.8750	26.25	Suggested
Cubic	0.5255	0.9908	0.9619	0.9508	10.34	Aliased

Table 5: Fit summary

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0.4226	0.0012	0.0010	-0.2858	
2FI	< 0.0001	0.0246	0.7375	0.6658	
Quadratic	< 0.0001	0.4937	0.9451	0.8750	Suggested
Cubic	0.2211	0.9329	0.9619	0.9508	Aliased

Table 6: Lack of fit

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Linear	179.02	20	8.95	23.81	0.0012	
2FI	34.24	14	2.45	6.50	0.0246	
Quadratic	4.09	10	0.4087	1.09	0.4937	Suggested
Cubic	0.0530	2	0.0265	0.0704	0.9329	Aliased
Pure Error	1.88	5	0.3760			

The "Predicted R²" of 0.8750 is in reasonable agreement with the "Adjusted R²" of 0.9451; i.e. the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 28.260 indicates an adequate signal. This model can be used to navigate the design space. The linear coefficient, quadratic coefficient and interactive coefficient with the exemption of X_2X_3 term significantly affects the % yield of the Lard oil based TMP ester [11].

The initial quadratic model for the % yield of lard oil based TMP ester;

TMP ester (%) = $+88.50 +0.5063X_1 -0.8588X_2 +0.3363X_3 +0.3279X_4 -0.8881X_1X_2 -2.32X_1X_3 -0.5381X_1X_4 -1.13X_2X_4 -1.13X_3X_4 -0.6628X_1^2 -0.6053X_2^2 -0.5191X_3^2 -0.6953X^2_4$.

The final quadratic regression model derived from the % yield of lard oil base TMP ester after eliminating the insignificant coefficient terms is;

TMP ester (%) = $+88.50 +0.5063X_1 -0.8588X_2 +0.3363X_3 +0.3279X_4 -0.8881X_1X_2 -2.32X_1X_3 -0.5381X_1X_4 +0.1756X_2X_3 -1.13X_2X_4 -1.13X_3X_4 -0.6628X_1^2 -0.6053X_2^2 -0.5191X_3^2 -0.6953X^2_4$.

The coefficient of regression R^2 was used to show how well the model can used to interpret the experimental data. The R^2 has a high value of 0.9716, implying that 97.16% of the variability in the response can be explained by the regression model. Table 7 shows a combination of the predicted and actual values of the experimental response from the regression model. There is a close correlation between the actual and predicted values of the response affirming the effectiveness of the synthesized lard oil based TMP ester.

Table 7: Actual and predicted values of lard oil based TMP ester % yield

Run Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residuals	Externally Studentized Residuals
1	80.20	79.88	0.3242	0.583	0.796	0.786
2	85.83	86.12	-0.2929	0.583	-0.719	-0.707
3	87.79	87.10	0.6937	0.583	1.704	1.833
4	93.00	92.48	0.5208	0.583	1.279	1.309
5	85.30	85.90	-0.6029	0.583	-1.481	-1.548
6	80.10	80.50	-0.3992	0.583	-0.980	-0.979

7	84.70	84.36	0.3387	0.583	0.832	0.823
8	86.25	86.32	-0.0658	0.583	-0.162	-0.156
9	87.59	87.80	-0.2063	0.583	-0.507	-0.494
10	85.67	85.43	0.2354	0.583	0.578	0.565
11	82.39	81.84	0.5454	0.583	1.340	1.379
12	87.80	88.50	-0.7000	0.167	-1.216	-1.237
13	88.60	88.50	0.1000	0.167	0.174	0.168
14	87.13	86.37	0.7554	0.583	1.856	2.042
15	87.00	86.86	0.1387	0.583	0.341	0.331
16	89.17	89.77	-0.5958	0.583	-1.464	-1.527
17	88.60	88.38	0.2154	0.583	0.529	0.516
18	88.30	88.50	-0.2000	0.167	-0.347	-0.337
19	85.96	86.37	-0.4129	0.583	-1.014	-1.015
20	87.45	87.09	0.3554	0.583	0.873	0.866
21	89.50	88.50	1.0000	0.167	1.737	1.877
22	83.56	83.57	-0.0092	0.583	-0.023	-0.022
23	86.71	86.98	-0.2729	0.583	-0.670	-0.658
24	88.66	88.83	-0.1742	0.583	-0.428	-0.416
25	84.44	85.06	-0.6229	0.583	-1.530	-1.609
26	84.83	84.84	-0.0063	0.583	-0.015	-0.015
27	88.00	88.50	-0.5000	0.167	-0.868	-0.861
28	88.80	88.50	0.3000	0.167	0.521	0.508
29	86.90	86.80	0.0992	0.583	0.244	0.236
30	85.19	85.75	-0.5613	0.583	-1.379	-1.425

Externally Studentized Residuals helps in the quantification of residues with respect to the standard deviation of the experimental data. It is an important technique in the identification of outliers and is calculated by leaving the outliers out of the analysis and estimating the response from the remaining experimental runs. The t value is the standard deviation difference between the predicted value and actual value of the response. It helps to test if the runs in question can interpret the model using coefficients estimated from the rest of the runs. The leverage of a point shows degree at which individual design point influences the models predicted value. The leverage of a point is in the range of 0 to 1, a leverage of 1 means that the predicted value is equal to the actual value of a particular experimental run, this invariably translate to a zero residual value. The sum of leverage for all experimental data is the sum of the number of co-efficient including constants. The normal plot of Residuals is used to check the linearity of the error term. The residual points should be approximately linear as a non-linear pattern such as a C-shaped curve indicates non-normality in the error term. The linearity of the residuals point shows a good correlation between the actual value and predicted value of the experiment, invariable implying that the generated regression model is adequate and can fully explain the experiment.

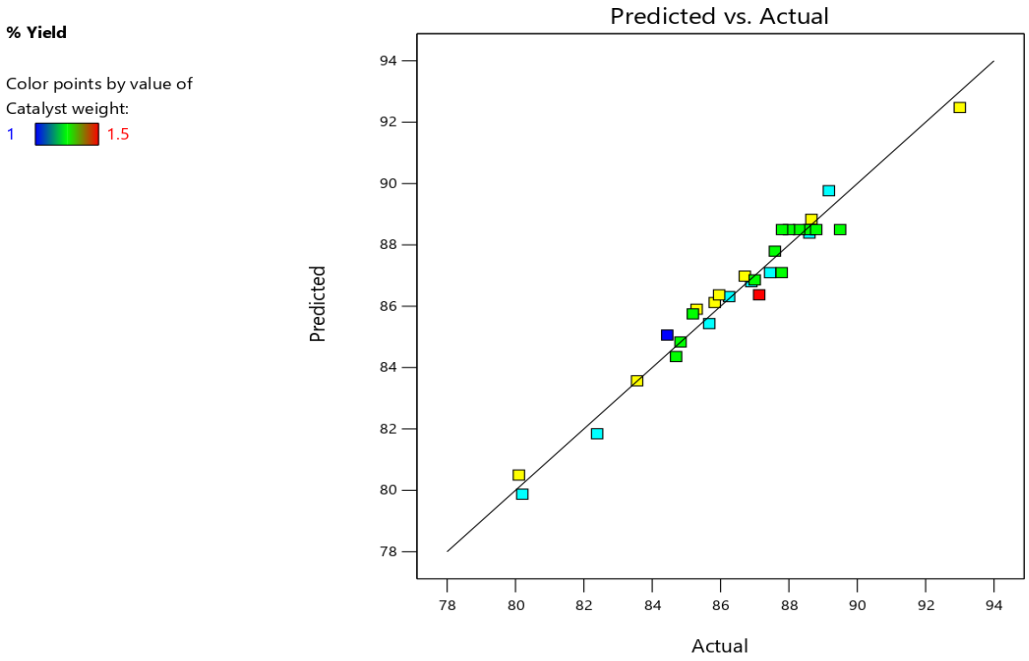


Figure 2: Predicted vs Actual plot for lard oil based TMP ester

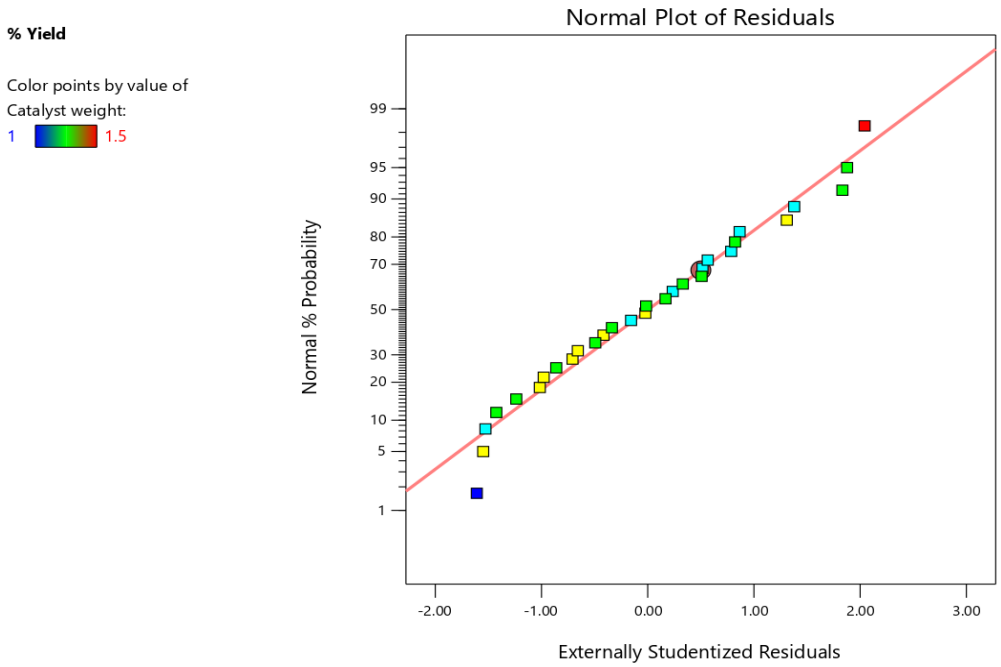


Figure 3: Normal plot of Residual for lard oil based TMP ester

3.3. Validation of the optimization result of lard oil based TMP ester

The experimental design was used to optimize the percentage yield of lard oil based TMP ester. The optimum value of 93% was achieved at a temperature of 130^{0}C, reaction time of 180 mins., catalyst weight of 1.5%w/w and molar ratio of 1:4 for a corresponding predicted value of 92.48%. To test the model, the experiment was repeated at optimal conditions and compared with the predicted value. The comparison of both the repeated experimental value

and predicted value showed a good agreement as the percentage error was less than 5%. Therefore, the design model obtained in this study can be used to explain the synthesis of lard oil based TMP ester.

Table 8: Validation of test result

Sample Predicted value (%)	Repeated Experiment (%)	% Error
TMP ester 92.48	93.3	0.9

Table 9: Properties of Lard oil based TMP ester in comparison with other biolubricants

Properties	Pour point	Flash point	viscosity@40^{o}C	viscosity@100^{o}C	Viscosity index	Specific gravity
Lard oil TMP ester	-10	229	40.51	10.22	232	1.10
Musa et al [12]	-8	215	45.3	9.21	191	-
Ocheje et al [13]	-21	196	35.55	7.66	193	-

3.4. Three Dimensional (3-D) response surface plots for lard oil based ester yield

The 3-D response surface plot for the TMP ester yield are shown in figures 4 to 6. The plots are graphical representation of the interactive effects of two variable factors. From Figure 4, the combined effects of molar ratio and temperature on TMP ester yield showed that an increase in molar ratio significantly increased the yield of the response by 8% from 81.4% to 83.6% while the increase in temperature merely increased the response yield by 2.7% from 81.4% to 83.6%. Similarly observation can be seen in Figure 5 and 6 where an increment in the variable factors of molar ratio, temperature, reaction time and catalyst weight caused a corresponding increment in the yield of the response.

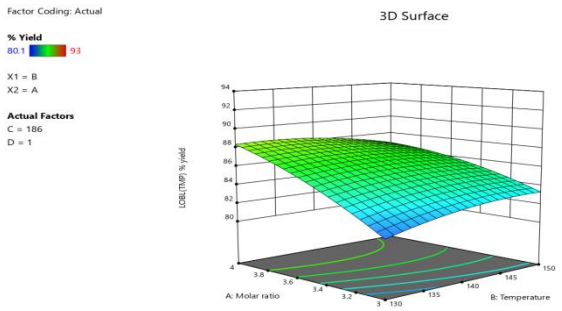


Figure 4: The combined effects of molar ratio and temperature on the % yield of TMP ester

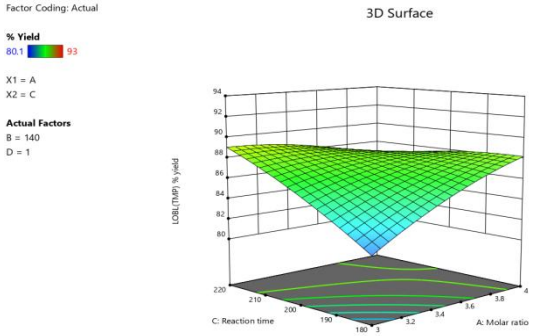


Figure 5: The combined effects of reaction time and molar ratio on the % yield of TMP ester

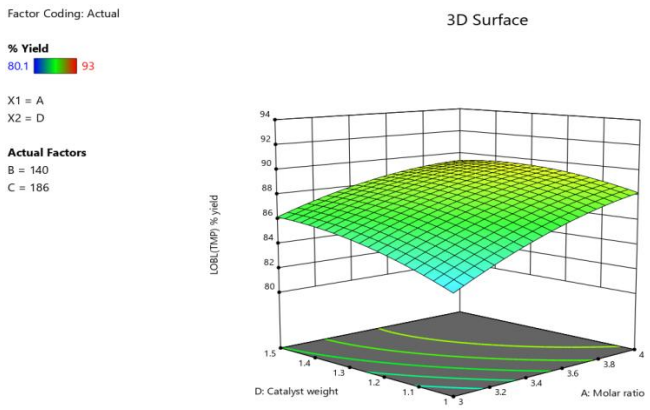


Figure 6: The combined effects of catalyst weight and molar ratio on the % yield of TMP ester

3.5. FTIR Analysis

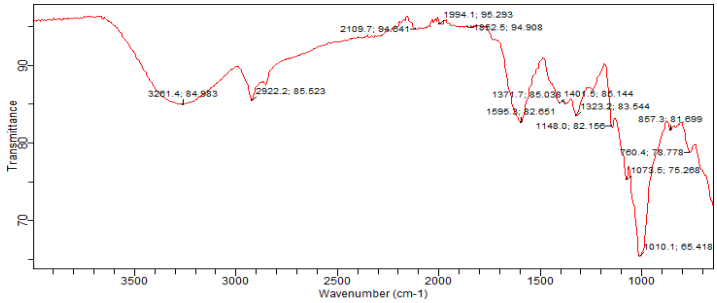


Figure 7: FTIR spectrum of lard oil TMP ester

The absorption band at the range 1595.3-1852.5cm^{-1} indicates the presence of the carbonyl (C=O) functional group, this suggest the formation of the lard oil TMP ester. Likewise the absorption band at 2922cm^{-1} is within the weak peak range for C-H stretching in the hydrocarbon component of the lard oil TMP ester which is a Sp3-hybridized carbon in alkanes. The weak broad peak at 3201.4cm^{-1} indicates the presence of O-H functional group showing the appearance of an alcohol and water molecules. This can be an indication that not all the TMP reacted with the methyl ester to form the biolubricant ester owing to the insufficient reaction time. The unreacted TMP and water molecules remained in the sample as impurities.

4. Conclusion

Lard oil based TMP ester was successfully synthesized from raw lard oil through a two stage transesterification processes. The optimum conditions generated by the central composite design model for the prediction of the % yield of the lard oil TMP ester were reaction temperature of 130^{0}C, mole ratio of 4:1, catalyst weight of 1.5%w/w and reaction time of 180 mins. The predicted TMP ester % yield was 93%. This study showed that the properties of the lard oil based TMP ester meets the ISO VG32 grade requirement and has its potential as a base oil for gear oil in automobiles.

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