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# Optimization of biodegradable lubricant basestock synthesis from Jatropha curcas seed oil using response surface methodology

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**Abstract**
This study was performed to optimize reaction parameters for the transesterification reaction of jatropha methyl ester (JME) and trimethylolpropane (TMP) using response surface methodology (RSM). The effects of five-level-threefactors and their reciprocal interactions were assessed. A total of 20 individual experiments were conducted and were designed to study reaction temperature, time and JME-to-TMP molar ratio. A statistical model predicted that the highest conversion yield of jatrophabiolubricant (JBL) would be 84.38%, at the following optimized reaction conditions: 150$^{o}$C, 200 min and a JME-to-TMP molar ratio of 5:1. At these optimum conditions, an average JBL yield of 82.74 ± 0.003% was achievedunder experimental conditions in three independent replicates, and this value was well within the range predicted (84.38%) by the model. The properties of JBL produced complied with International Organization for Standardization Viscosity Grade 32 (ISO VG 32) standard and could be applied as lube base-stock with minor modifications.

**Keywords:**Jatropha, biolubricant, transesterification, trimethylolpropane, response surface methodology

**NOMENCLATURE**

| | |
|---|---|
| ANOVA | Analysis of variance |
| ASTM | American System of Testing and Materials |
| CCD | Central Composite Design |
| DE | Diesters |
| DG | Diglycerides |
| FAME | Fatty acid methyl esters |
| FTIR | Fourier transform infra-red |
| GC | Gas chromatography |
| ISO | International Organization for Standardization |
| JBL | Jatropha biolubricant |
| JME | Jatropha methyl ester |
| LEAR | Low erucic acid rapeseed |
| ME | Monoester |
| MG | Monoglyceride |
| NPG | Neopentyl glycol |
| PE | Pentaerythritol |
| RSM | Response surface methodology |
| TE | Triester |
| TG | Triglyceride |
| TMP | Trimethylolpropane |
| VG | Viscosity Grade |
| VI | Viscosity Index |

## 1. Introduction

Biolubricants produced from vegetable oils and animal fats provide a good alternative tones sourced from fossil fuel (Altin et al, 2001). The finite nature of fossil fuelsand increased awareness of environmental pollution by petroleum-based oils for use as industrial lubricants arepart of major reasons for the ongoing drive towards the alternative use of more environmentally friendly vegetable oil as lube basestock(Dincer, 2008; Sigar et al, 2009). Lubricants' production from renewable resources, such as vegetable oils and animal fats, ensures lubestocks are biodegradable and non-toxic.It also contributes to the reduction of $CO_2$ emissions, due to the presence of a closed carbon cycle in these fats and oils(Bozbas, 2009; Van, 2005). There is a great concern regarding the use of food oils for the production of biolubricant and accordingly, studies are being conducted to use non-edible oils, as well as by-products from the refining of the vegetable oils (Veljkovic et al, 2006). Fatty acids polyol esters of vegetable oils (triglyceride) are untreated naturally occurring feedstock with high lubricity potential that could be modified (by transesterification) into environmentally friendly, rapidly biodegradable and renewable base stock for lubricant (Wagner et al, 2001).

Commonly, bio-lubricant has been manufactured by acid or base-catalyzedtransesterification of fatty acid methyl esters (FAME), typically methylethanoate, with polyhydric alcohol such as trimethylolpropane (TMP)(2-ethyl-2-hydroxymethyl-1,3-propanediol),neopentyl glycol (NPG) and pentaerythritol (PE) (Asadauskas, 2000; Doson, 1979; Erhan andPersson, 2000). Several synthetic approaches are available for the transesterification reaction between FAME and polyol(in this report TMP), which produces polyolester(in this report TMPester). Such reactions have been classified by the catalysts used in the reactions. These catalysts could be acid, base or enzyme and would catalyze both esterification and transesterification reactions (Schuchardt et al, 1998). Thetransesterification route is mature with a good measure of success and acceptance due to the high conversion efficiency of FAME to polyol ester. For example, it has been reported that 99% of TMP was successfully converted to triester (TE) in the transesterification reaction of low erucic acid rapeseed (LEAR) oil methyl ester with TMP (Uosukainen et al, 1998). In this reaction, 0.5% sodium methoxide was used to catalyze the reaction of a 3.3mole ratio of LEAR oil methyl ester to TMP at 110 – 120$^{o}$C for 10h under 3.3kPa pressures. Subsequently, Yunus et al. (2003) optimized the reaction time and produced 98% TMP TE with 0.9% sodium methoxide as the base catalyst at 130$^{o}$C for 1h at a pressure of 20mbar and the 3.9moleratio of palm kernel oil methyl esters to TMP.

An improved two-step transesterification process for producing higher polyol (sucrose) fatty acids polyesters (Volpenhein and Ohio, 1985) was developed. In the first step of the reaction, high conversion to polyol esters (90%) was achieved by using potassium carbonate as the base catalyst, while 85% conversion was obtained by using sodium methoxide. The ratio of FAME to sucrose in the first reaction was 4.75 and in the second reaction stage was 7.98. Therefore, this base-catalyzedtransesterification was efficiently achieved using a safer and less expensive base catalyst (potassium carbonate) to obtain a high percentage of conversion. In this study, a novel(by employing heterogeneous catalyst to drive the process)synthetic approach for transesterification reaction of Jatropha Methyl Ester (JME) with trimethylolpropane-catalyzed by calcium hydroxide is presented.

The use of heterogeneous catalyst offered the advantages of no soap production as a by-product and easy separation of catalyst from the reaction products). It is undertakento produce jatrophabio-lubricant (JBL) in which the major objective was to optimize, using response surface methodology (RSM), the process variables influencing the transesterification reaction.RSM has been applied in many process optimizations such as biodiesel production, adsorption processes, synthesis of oleochemicals and catalyst development (Jiang and Niu, 2011, Ghadge and Raheman, 2006). However, there are scarce reports on the optimization of trimethylolpropane based biolubricant synthesis (Sun *et al.*, 2011, Naidir *et al.*, 2011). Moreover, although Jatropha seed has been used as a starting material for biolubricant synthesis via transesterification reactions (Kaushik et al, 2007; Gubizet al, 1997; Muhammad et al, 2011; Mohamad et al, 2012; Ghazi et al, 2009), the process, to the best of our knowledge, has not yet been optimized using a statistical approach such as response surface methodology.

In this study, we present a novel synthetic approach for transesterification reaction to produce a high yield of biolubricant by optimizing the reaction process variables. The process variables studied using response surface methodology (RSM) were temperature, mole ratio and time. RSM design was applied to relate these three process variables with the response (JBL yield %). Furthermore, the Fourier transform infra-red (FTIR) was analyzed and physicochemical properties of the product were also studied.

## 2 Materials and Methods

### 2.1. Materials

*Jatrophacurcas*samples were collected from Idah, Kogi State, Nigeria. The seeds were cleaned, shelled and air-dried in the shade for two weeks. All the chemicals and reagents used for this work were of analytical grade.

### 2.2. Extraction of oil from *Jatropha* Seed

Dried Jatropha seeds were crushed and tied in a white piece of cloth. This was later soaked in hexane in a tightly sealed bucket for 3 days before collecting the extract through filtration. The cloth containing the crushed *Jatropha* seeds was further rinsed with fresh hexane to extract more oil. Hexane contained in the extracted jatropha oil was removed by distillation and the crude oil extract was collected in a beaker (Menkiti et al, 2015; Ocholi et al, 2017).

### 2.3. Synthesis of *Jatropha* Methyl Ester

Jatropha oil extracted from jatropha seed was transesterifiedusing methanol to form Jatropha Methyl Ester (JME). In this method, a mixture of 300g of jatropha oil, 100g methanol and 1% wt/wtorthophosphoric acid catalyst was poured into a continuously stirred reactor equipped with a water-cooled reflux condenser and heated up to 65$^{o}$C for 90 min. The mixture was dosed with 0.2 molar solution of sodium trioxocarbonate IV, which on neutralizing the acid catalyst, stopped the reaction. The neutralized mixture was later transferred to a separating funnel and subsequently allowed to stand overnight to ensure complete separation of methyl esters and glycerol phases. Glycerol phase (bottom phase) was emptied into a clean container and then allowed to stand. The obtained *jatropha* methyl ester washeated to and kept at 65°C until the entrained methanol was removed. Entrained catalyst in the JME was removed by successive rinsing with hot and distilled water. Finally, water present in the JME was eliminated by oven-heating at 70°C (Menkiti et al, 2015; Ocholi et al, 2017).

### 2.4. Synthesis of *Jatropha* Biolubricant

This was as described by Surapoj, et al., (2013) with modifications (see Plate 2.1). A batch transesterification at predetermined conditions: TMP:JME (3:1, 4:1, 5:1, 6:1 and 7:1), temperature (80, 100, 120, 140 and 160 $^{o}$C) and time (1, 2, 3, 4 and 5h) was carried out in a 50-mL three-necked round bottom flask equipped with a water-cooled reflux condenser, a thermometer, kipp's apparatus and a magnetic stirrer. The kipp's apparatus was used for $CO_2$ synthesis which provided inert atmosphere for the transesterification reaction. The entire experimental setup is thus presented in plate 3.1. The reactionmixture contained in the flask was stirred at 1000 rpm, 110 °C for 15 min under $CO_2$ flow. 110°C was maintained to evolve moisture from the TMP. A required amount of catalyst (1 wt% of the reaction mixture) was then introduced in the reaction mixture, which was allowed to react for 5 h. At the end of the reaction, the product mixture was brought to room temperature and filtered to separate the solid catalyst from the liquid mixture (JBL). The filtered jatropha bio-based stock was analyzed using the Gas chromatography (GC) to determine the product composition. Pour point, viscosity, flash point and viscosity index were also determined by appropriate analysis (Menkiti et al, 2015; Ocholi et al, 2017).

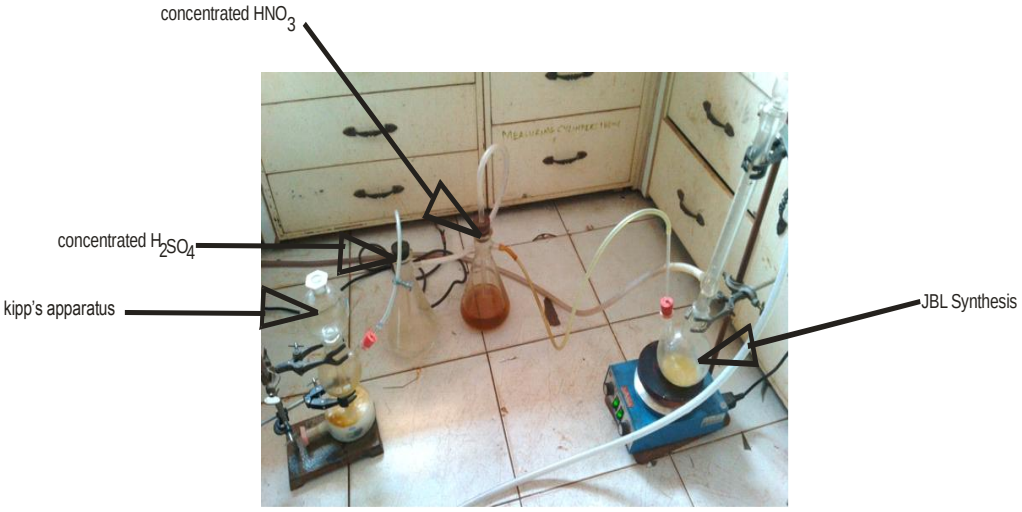


**Plate 2.1: Experimental setup for the Kipps apparatus**

### 2.5. Analysis of Transesterification Product

Identification of functional groups present in JBL was determined using Fourier Transform Infrared (FTIR) Resonance. Samples were collected at 1h, 2h, 3h, 4h and 5h and analyzed for JME, monoester (ME), diesters (DE), triesters (TE) and TMPby gas chromatography (GC). The yield of each product was determined from the GC chromatogram calibrated against the known samples according to the procedure described by Yunus et al. (2002).

### 2.6. Lubricating Characteristics

The following lubricating characteristics were determined based on the corresponding referred American System of Testing and Materials (ASTM) procedures: Pour Point ASTM D97- 17a (ASTM, 2017); Kinematics Viscosities ASTM D445 - 17a (ASTM, 2017); Viscosity Index, ASTM D2270 - 10(2016) and Flash Point (ASTM, 2013).

### 2.7. Design of experiment

The Central Composite Design (CCD) was used to study the effects of the variables of the transesterification reaction and subsequently in the optimization of the process. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters. To describe the effects of temperature, time and mole ratio on the yield of biolubricant, batch experiments were conducted based on the CCD. The coded values of the process parameters were determined by Eq. (1).

$$x_i = \frac{X_i - X_o}{\Delta X} \quad (1)$$

where$x_i$ – coded value of the ith variable, $X_i$ – uncoded value of the $i^{th}$ test variable and $X_o$ – uncoded value of the ith test variable at center point. A second-order polynomial (Eq. 2) was used to express the biolubricant yield (Y) as a function of the independent variables,

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ij} X_i^2 + \sum_{i_1<j}^{k} \sum_{j}^{k} b_i X_i X_j + e \quad (2)$$

WhereY is response factor (% yield), and i and j denote linear and quadratic coefficients, respectively. $b_o$ is the intercept, $b_i$is the first-order model coefficient, k is the number of factors, and e is a random number. The Factors levels of independent variables for JBL synthesis is given in Table 1.

**Table 1: Factors levels of independent variables for JBL synthesis**

| Independent Factors | -α | Low level (-) | Medium level (0) | High level (+) | +α |
|---|---|---|---|---|---|
| Temp, $^oC$ | 123.82 | 130 | 140 | 150 | 156.818 |
| Time, min | 146.364 | 160 | 180 | 200 | 213.636 |
| Mole ratio | 2.31821 | 3 | 4 | 5 | 5.61879 |

The regression analysis was performed to estimate the response function as a second-order polynomial. The tests for adequacy of the regression models, values and significance of individual model coefficients and the lack of fit test were performed using a statistical program package, Design Expert 8.7.0.1.Analysis of variance (ANOVA) was further carried out to justify the adequacy of the model. The significance of each term in the equation is to estimate the goodness of fit in each case. Response surfaces were drawn to determine the individual and interactive effects of the test variable on the yield of biolubricant. The optimal values of the test variables were first obtained in coded units and then converted to the uncoded units. The high (+) and low (-) values for TMP ester synthesis were temp (130 and 150$^o$C), time (160 and 200min) and mole ratio (3.0 and 5.0). The alpha (α) value used was 1.414. Table 2 shows the complete design matrix of the experiments carried out, together with the results obtained.

## 3. Results and discussion

### 3.1. Optimisation of the Process Parameters Using Response Surface Analysis

#### 3.1.1. Model Fitting and Analysis of Variance (ANOVA)

RSM is a useful tool for modelling and analysis of the response of interest when the response is influenced by several variables and the objective is to optimize these responses (Montgomery *et al*., 2001). The optimization process of the transesterification reaction was done using the Central Composite Design (CCD). Three important factors which are temperature, time, and mole ratio were used as the independent variables. Their combined effects

were examined while the percentage yield of the biolubricant was the dependent variable or the response. This was done to determine the best conditions for the optimum yield of biolubricants. Using the CCD involves varying the independent variables at five different levels (-α, -1, 0, +1, +α). In this work, a set of 20 experiments were performed including 6 centre points of null points. The distance of the star-like point, α, used was 1.412. The experiments were performed at random to avoid a systematic error. The mole ratioof JME:TMP used for the process was in the range of 4 and 6, temperature between 130 and 150$^{o}$C, time ranged between 160 and 200 minutes, based on the results of the batch studies. The central composite design arrangement and response for JBL synthesis considered in this work are shown in Table 2. The normal plot of residuals (Figure 1) and the predicted vs actual plot for JBL synthesis (Figure 2) showed a satisfactory correlation between the actual and predicted values of JBL yield.

**Table 2: Central composite design arrangement and response for JBL synthesis**

| Run | A=Temperature | B=Time | C=Mole ratio | Percentage yield | Predicted Value |
|---|---|---|---|---|---|
| 1 | 130 | 200 | 3 | 71.49 | 68.77 |
| 2 | 150 | 160 | 3 | 72.31 | 71.15 |
| 3 | 140 | 180 | 4 | 80.12 | 72.87 |
| 4 | 150 | 200 | 5 | 74.99 | 74.56 |
| 5 | 140 | 180 | 4 | 77.2 | 76.86 |
| 6 | 140 | 180 | 2.32 | 81.32 | 80.17 |
| 7 | 140 | 180 | 4 | 80.37 | 81.76 |
| 8 | 140 | 180 | 4 | 82.74 | 84.38 |
| 9 | 140 | 213.64 | 4 | 77.93 | 77.43 |
| 10 | 123.18 | 180 | 4 | 81.46 | 81.63 |
| 11 | 150 | 200 | 3 | 70.26 | 72.78 |
| 12 | 130 | 160 | 5 | 82.6 | 79.76 |
| 13 | 140 | 146.36 | 4 | 65.83 | 66.31 |
| 14 | 140 | 180 | 4 | 82.18 | 81.37 |
| 15 | 130 | 200 | 5 | 80.73 | 80.35 |
| 16 | 140 | 180 | 4 | 79.62 | 80.35 |
| 17 | 156.82 | 180 | 4 | 81.2 | 80.35 |
| 18 | 130 | 160 | 3 | 79.59 | 80.35 |
| 19 | 140 | 180 | 5.68 | 80.12 | 80.35 |
| 20 | 150 | 160 | 5 | 81.32 | 80.35 |

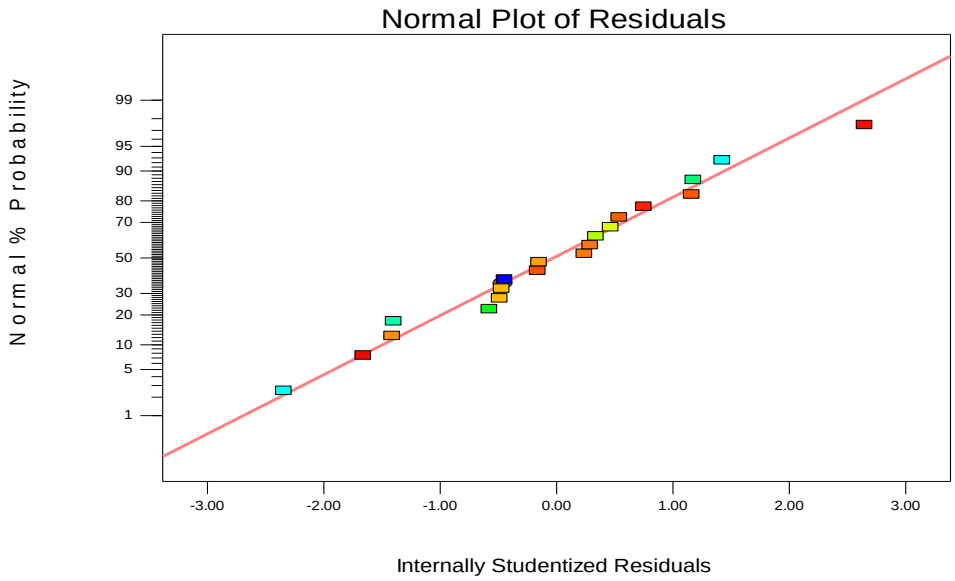


**Figure 1: Normal Plot of Residuals for JBL synthesis**

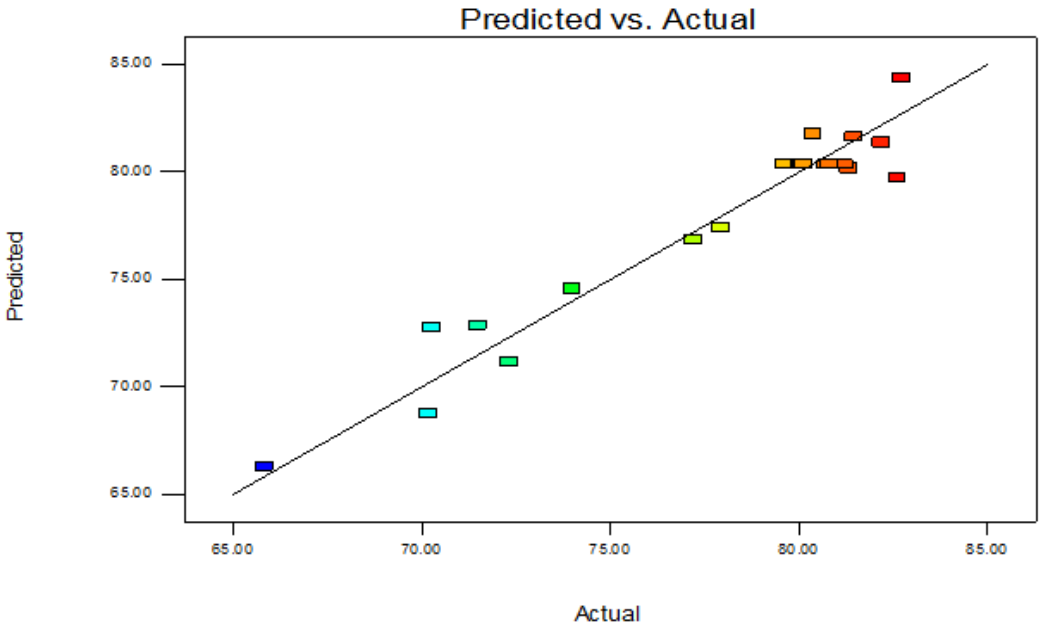


**Figure 2: Predicted Vs Actual plot for JBL synthesis**

A quadratic polynomial equation was obtained from the experimental data to predict the biolubricant yield is shown in Eq. (3) below in terms of coded variables.

$$Yield_{JBL}(\%) = +80.35 + 1.25A + 2.08B + 4.48C - 0.17AB + 0.23AC + 0.20BC - 0.29A^2 - 1.45B^2 - 2.30C^2 \quad (3)$$

In a regression equation, when an independent variable has a positive sign, it means that an increase in the variable will cause an increase in the response while a negative sign will result in a decrease in the response (Russell, 2009). Hence, an increase in temperature, time, and mole ratio will cause an increase in the percentage yield. Time and mole ratio will have a more significant effect on the increment of the response since their coefficients were higher.

Table 3 shows the results of the analysis of variance (ANOVA) for all the regression coefficient.

**Table 3: ANOVA for JBL synthesis**

| Source | Sum of Squared | Df | Mean Square | F-value | p-value prob > F | Remarks |
|---|---|---|---|---|---|---|
| Model | 453.11 | 9 | 50.35 | 17.14 | < 0.0001 | Significant |
| A-Temp | 21.33 | 1 | 21 | 7.26 | 0.0225 | |
| B-Time | 58.82 | 1 | 58.82 | 20.02 | 0.0012 | Significant |
| C-Mole ratio | 273.96 | 1 | 273.96 | 93.25 | < 0.0001 | Significant |
| AB | 0.24 | 1 | 0.24 | 0.082 | 0.7802 | |
| AC | 0.43 | 1 | 0.43 | 0.15 | 0.7107 | |
| BC | 0.32 | 1 | 0.32 | 0.11 | 0.7497 | |
| $A^2$ | 1.22 | 1 | 1.22 | 0.42 | 0.5335 | |
| $B^2$ | 30.11 | 1 | 30.11 | 10.25 | 0.0095 | |
| $C^2$ | 76.43 | 1 | 76.43 | 26.01 | 0.0005 | Significant |
| Residual | 29.38 | 10 | 2.94 | | | |
| Lack of Fit | 27.14 | | 55.43 | 12.11 | 0.0080 | |
| Pure Error | 2.245 | 0.45 | | | | |
| Cor Total | 482.49 | 19 | | | | |

| | | | |
|---|---|---|---|
| Std. Dev. = 1.71 | Mean = 77.60 | C.V. = 2.21 % | PRESS = 210.25 |
| R-Squared = 0.9391 | Adj. R-Sq. = 0.8843 | Pred. R-Sq. = 0.8642 | Adeq. Precision = 14.906 |

The results indicated that the model terms: the three linear terms (A, B, C), and two quadratic terms ($B^2$ and $C^2$) were significant at a 95% confidence level since $p < 0.05$.The P values were used as a tool to check the significance of each of the coefficients, which in turn were necessary to understand the pattern of the mutual interactions between the test variables (Kumar et al, 2003; Ocholi et al., 2017). Moreover, the effect of these parameters on yield can be observed by looking at the respective F-value and P values shown for each parameter in Table 3. The higher the F-value (and lower the P values), the more pronounced the effect of the said parameter will be on the yield. The model also proved suitable for adequate representation of the real relationship among the selected independent variables (A, B, C).

**Table 4:Summary of *P*-values for JBL synthesis**

| Source | Sequential p-value | Lack of Fit p-value | Adjusted R-Squared | Predicted R-squared | Remarks |
|---|---|---|---|---|---|
| Linear | < 0.0001 | 0.0011 | 0.6840 | 0.5837 | Not suggested |
| 2FI | 0.9914 | 0.0006 | 0.6141 | 0.2483 | Not suggested |
| Quadratic | 0.0016 | 0.0080 | 0.8843 | 0.8642 | Suggested |
| Cubic | 0.0023 | 0.4728 | 0.9835 | 0.8700 | Aliased |

The model F value of 17.14 with a low probability value ($p < 0.0001$) implied a high significance for the regression model (Honary, 2001; Yuan et al., 2008). The goodness of fit of the model was checked by the coefficient of determination ($R^2$), Which should be close to unity for the good fit of a model (Stuart, 2004). The $R^2$ value of 0.9391 indicated that the sample variation of 93.91% for biolubricant was attributed to the independent variables, and only 6.09% of the total variations are not explained by the model.

**Table 5: Summary of Model Statistics for JBL synthesis**

| Source | Std. Dev | R-Squared | Adjusted R-Squared | Predicted R-squared | PRESS | Remarks |
|---|---|---|---|---|---|---|
| Linear | 2.83 | 0.7339 | 0.6840 | 0.5837 | 200.88 | Not suggested |
| 2FI | 3.13 | 0.7360 | 0.6141 | 0.2483 | 362.70 | Not suggested |
| Quadratic | 1.71 | 0.9391 | 0.8843 | 0.8642 | 210.25 | Suggested |
| Cubic | 0.65 | 0.9948 | 0.9835 | 0.8700 | 62.74 | Aliased |

The value of the adjusted determination coefficient (adjusted $R^2$ of 0.8843) was also close to unity, supporting a high significance of the model (Rao et al., 2012; Salimon et al., 2010). The summary of P-values statistics is shown in Table 4. A quadratic model was suggested from the CCD module. The cubic model is always aliased because the CCD does not contain enough runs to support a full cubic model. A significance level of 95% was used hence all terms whose P-value are less than 0.05 were considered significant. The model summary test for the synthesis of biolubricant are also presented in Table 5. The final equation in terms of coded factors for the central composite response surface quadratic model, after removal of insignificant terms, is expressed in Eq. (4).

$$Yield_{JBL}\ (\%) = 80.35 + 1.25A + 2.08B + 4.48C - 1.45B^2 - 2.30C^2 \quad (4)$$

To observe the interaction of the process variables (temperature, mole ratio and time), 2D contour plots are presented in Fig. 3–5.

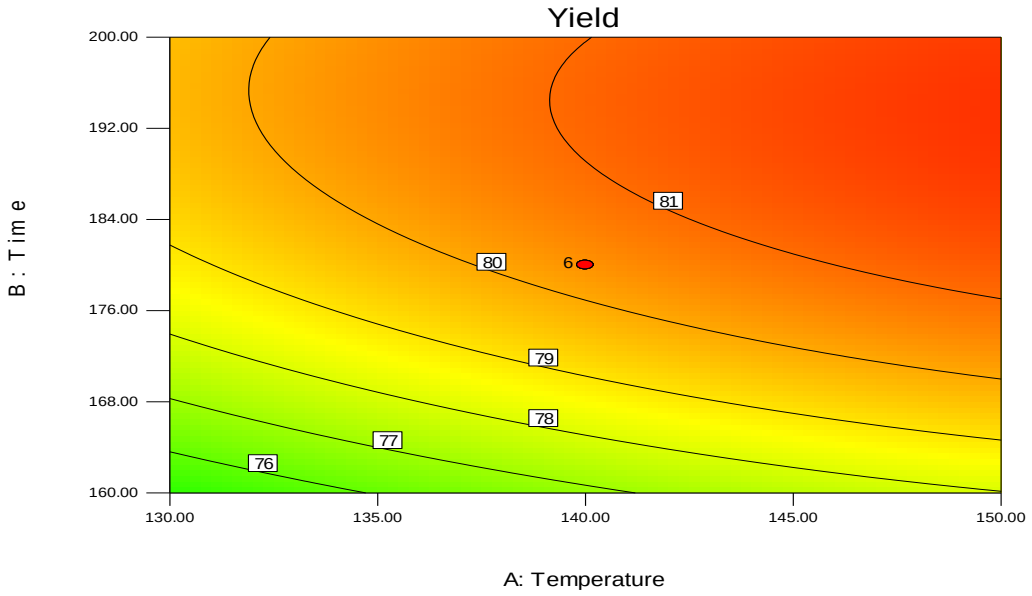


**Figure 3: 2D surface plot for effect of temperature and time on JBL yield**

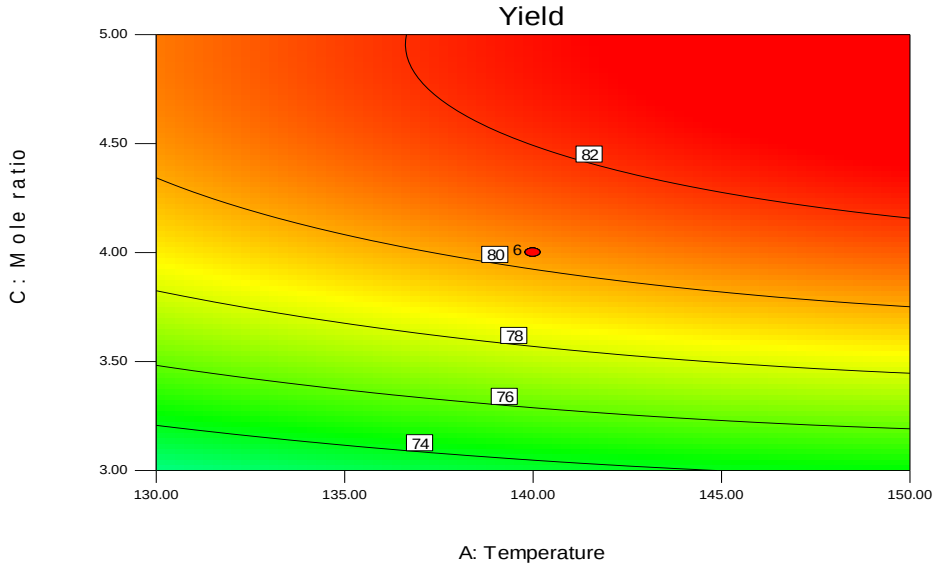


**Figure 4: 2D surface plot for effect of temperature and mole ratio on JBL yield**

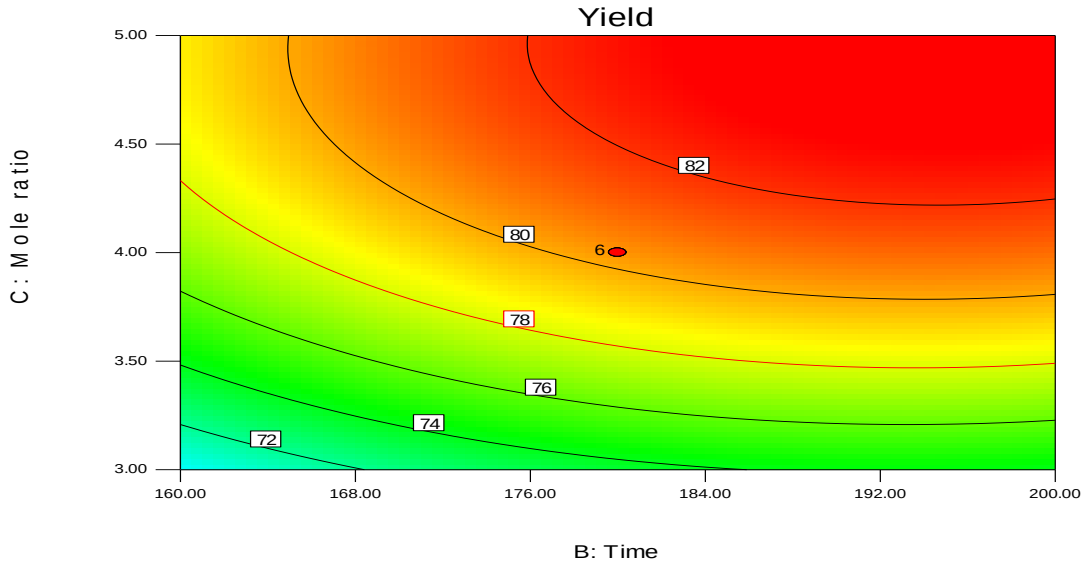


**Figure 5: 2D surface plot for effect of mole ratio and time on JBL yield**

The optimized response was determined when the interaction of the two process variables were studied while one was kept constant. The predictor estimated that The TE yield was found to vary between 65.83 and 82.74 wt % for JBL (Figures 3–5). Fig. 3 has indicated a plot of the process variables that gave the most significant impact to the fitted model was the interaction between the temperature and time. It could be seen that increasing the temperature and time significantly increased the JBL yield. The increment of temperature and mole ratio raised the JBL yield as shown in Figure 4. Mole ratio had a more significant effect on the increment of the response than temperature. The reason might be due to the volatilization of the JME component during the reaction at a higher temperature when a reversed reaction could not be prevented (Yunus et al., 2003). Nevertheless, at a high temperature, there was an increment of the JBL composition which resulted from the methanol produced from the reaction. (Ocholi et al, 2017). Figure 5 depicts the interaction between the mole ratio and the reaction time. The JBL composition increased as the mole ratio and reaction time increased. Generally, the 3D response surface plots are graphical representations of the regression equation for the optimization of the reaction variables. Figures 6-8 indicate 3D response surface plots showing the effect of process parameters on biolubricant yield.

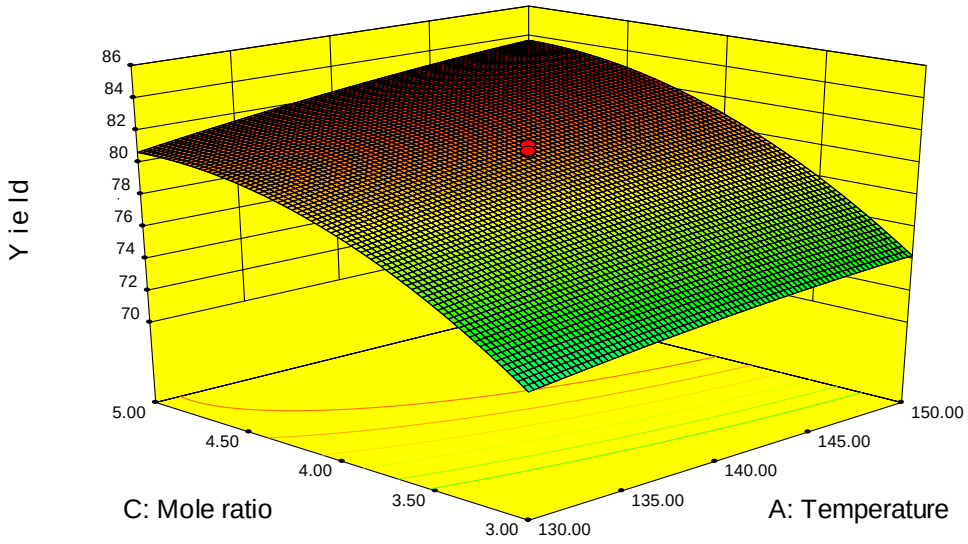


**Figure 6: Surface and contour plot between mole ratio and temperature against JBL yield**

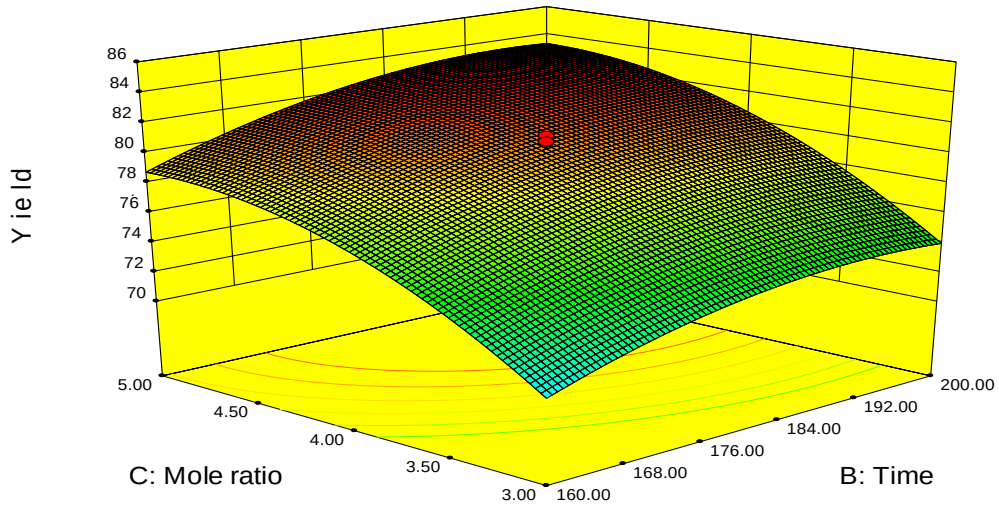


**Figure 7: Surface and contour plot between mole ratio and time against JBL yield**

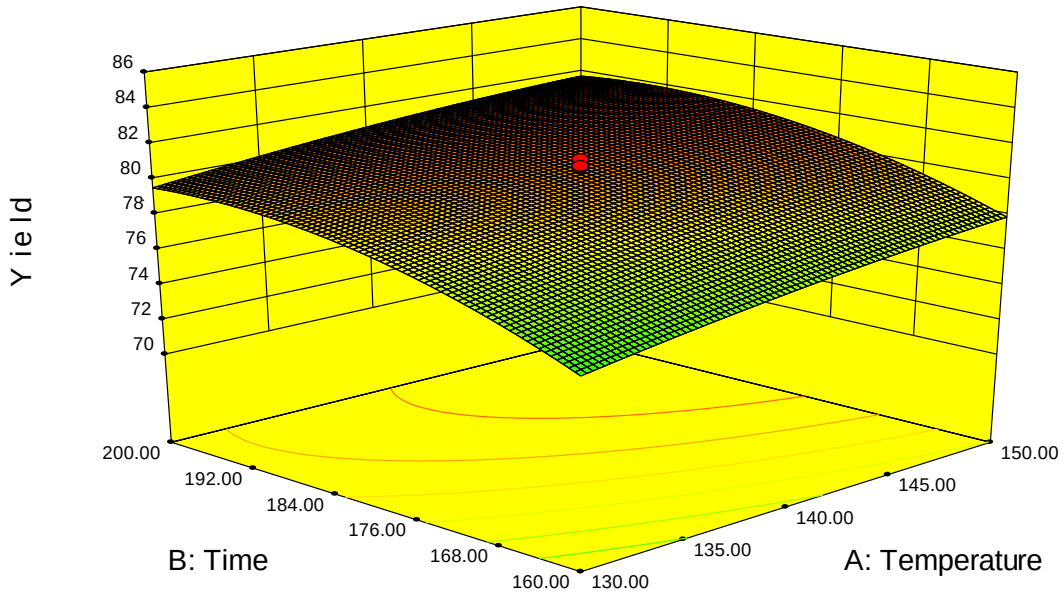


**Figure 8: Surface and contour plot between time and temperature against JBL yield**

The response surface of the extent of conversion showed a clear peak, suggesting that the optimum condition for maximum yield (Y) was well inside the design boundary. It could be observed that the conversion increased when the molar ratio and temperature were increased. It was observed that for temperature, yield (Y) increased with increasing mole ratio until 4.5:1 JME to TMP mole ratio (Figure 6), where, for lower values of temperature the pattern followed a parabolic path. At a fixed value of the molar ratio, the increase in temperature increased the value of the yield (Y) until about 140$^{o}$C after which there was no significant increase in yield (Figure 8). Figures 6-7 indicate that the biolubricant synthesis increased when FAME concentration increased. Therefore, an increase in FAME to TMP mole ratio enhanced biolubricant conversion. Generally, a better product yield was obtained by keeping the molar ratio of reactants higher than the stoichiometric values since the reaction was driven more towards completion. Thus, an excess FAME could be used to drive the reaction near completion. Consequently, the FAMEconcentration results in a greater biolubricant conversion within a shorter time as indicated in Figure 6. The mole ratio (FAME/TMP) is a fundamental variable in the transesterification process for biolubricant synthesis (Ocholi et al, 2017; Sripada, 2012).

Figures 6 and 8 explain the effect of varying reaction temperature on the response. The temperature has a steady positive but moderate effect on biolubricant yield. It was revealed that an increment of reaction temperature led to an increase in biolubricant yield with reduced time. However, increasing reaction time did not improve the catalytic activity at a low-temperature level. Meanwhile, high temperature improved the dispersion of catalyst particle in liquid medium with better mass transfer between the reactants. The contour plot showsthat high biolubricant yield was favoured by a higher level of reaction temperature with a low or intermediate level of reaction time. However, an increase in reaction time did not have a significant effect on the yield after about 3 hours of reaction (Ocholi et al., 2017).

3.1.2. Process variable optimization and validation procedure

The optimal values of the selected variables were obtained by solving the regression equation (Eq. (3)) using Design-Expert 8.7.0.1 software. The optimal conditions for JBL synthesis estimated from the model equation were as follows: A =150$^{o}$C, B = 200 min and C = 5:1 (Table 6).

**Table 6: Optimization/Validation Results for JBL Synthesis**

| Parameter | Optimum operating condition |
|---|---|
| Temperature ($^{o}$C) | 150 |
| Time(min) | 200 |
| Mole ratio | 5:1 |
| Yield (optimum) wt% | 84.38 |
| Yield (Validated) wt% | 82.74±0.03 |

At these conditions, a TE yield of 84.38 wt% was obtained at a desirability value of 1.00. Figure 9 shows surface and contour plots for desirability, wherein desirability is plotted against temperature and mole ratio, respectively at a fixed time of 200 min, while Figure 10 shows a 3D contour plot for desirability against temperature and mole ratio for SBL synthesis.

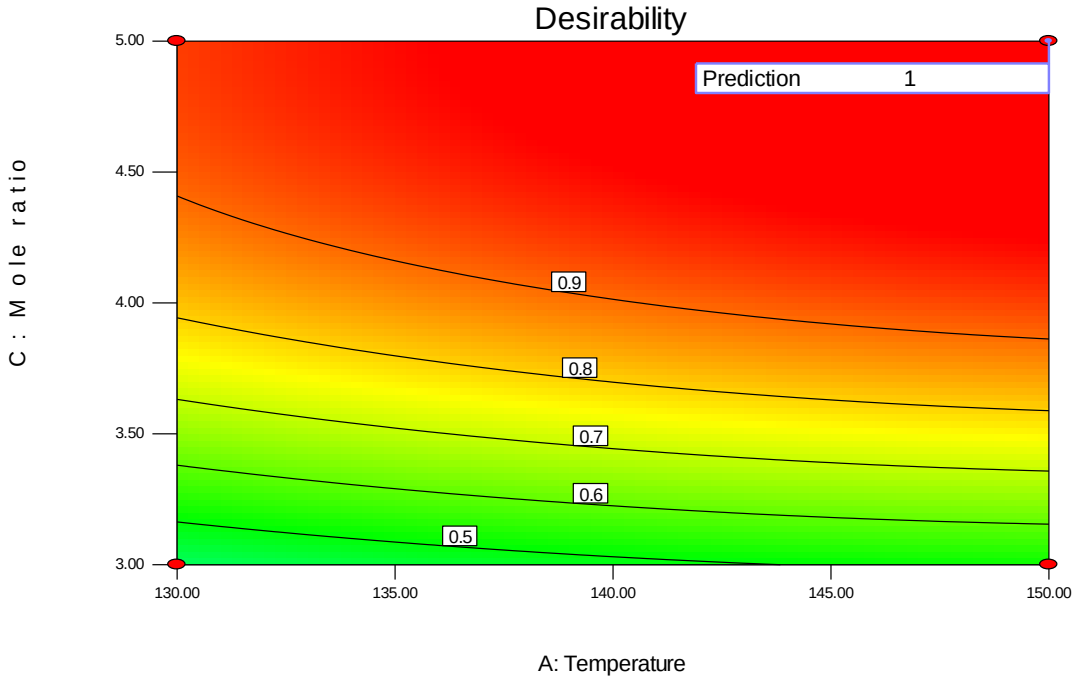


**Figure 9: 2D surface plot for desirability against temperature and mole ratio for JBL**

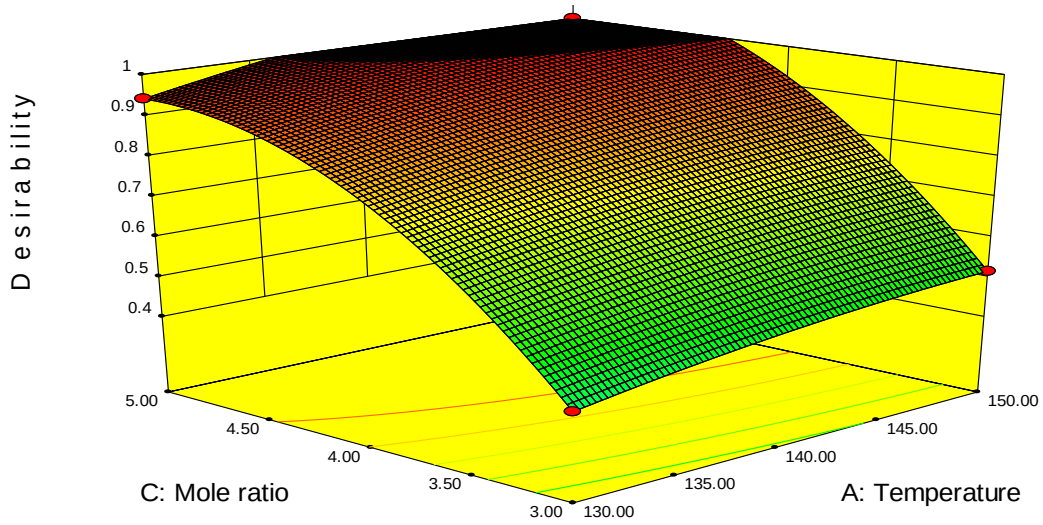


**Figure 10: 3D contour plot for desirability against temperature and mole ratio for JBL synthesis**

Sripada, (2012) applied this method to the transesterification reaction between methyl oleate and TMP and determined the optimum condition to be temperature of 139$^{o}$C, mole ratio 4.9 and catalyst loading of 1.42 wt % and obtained a TE yield of 91.2 wt %.Yunus et al., (2003) determined the optimum synthesis conditions for maximum conversion of palm oil methyl esters to TMP triester to be the temperature of 130$^{o}$C, the vacuum pressure of 20 mbar, 3.9:1 palm oil methyl esters / TMP mole ratio for 0.8% w/w sodium methoxide catalyst.Ghazi et al., (2009) utilized a temperature of 150$^{o}$C, with a pressure of 10 mbar, mole ratio of JME-to-TMP ratio of 4:1.

To verify the prediction of the model, the optimal reaction conditions were applied to three independent replicates for JBL synthesis. The average conversion yield was 82.74 ± 0.03%, a figure well within the estimated value of the model equation. Figure 2 shows a comparison plot of predicted versus actual values, which indicated that the relationship between modelled and experimental values was excellent.Figure 11 shows plots for standard error of design as a function of temperature and time. The plot (Figure 11) shows that the data for biolubricant synthesis experiment are within 95% confidence level.

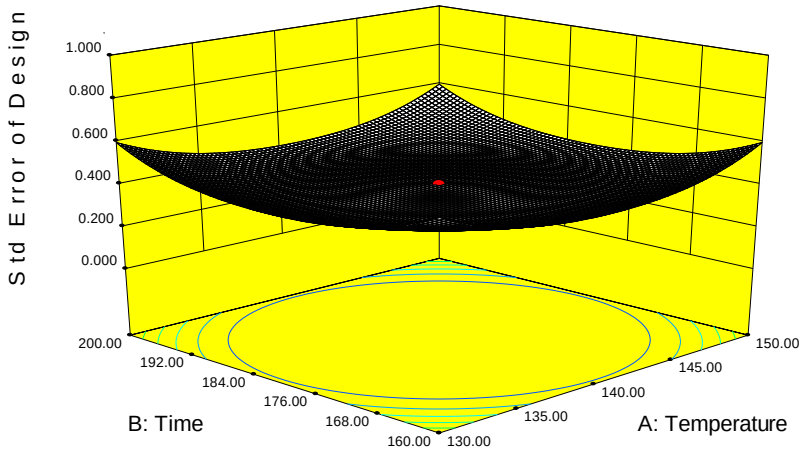


**Figure 11: 3D contour plot for standard error of design as a function of temperature and time (JBL)**

Studies were performed to check for the reproducibility of data obtained from transesterification reactions for the synthesis of JBL. The centre point experiment was performed 6 times as indicated by the CCD model. The final TE yield varied between 79.59 and 81.20 wt %. Figure 12 shows scatter plots of the six experiments at the centre point.

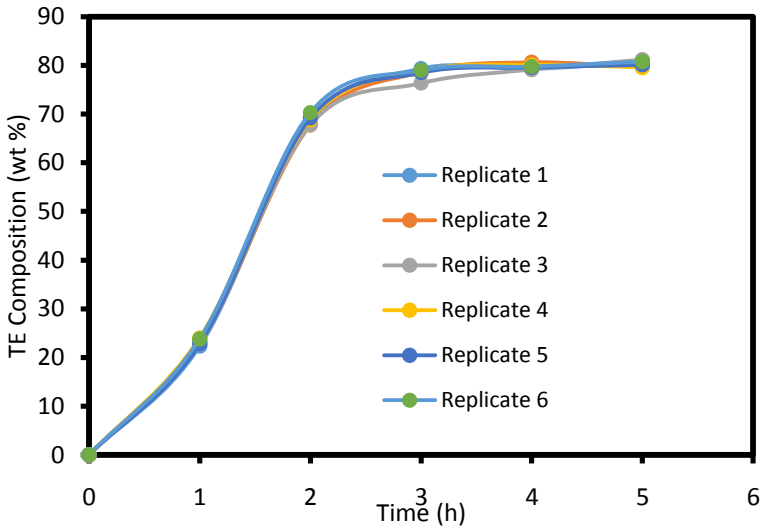


**Figure 12: Scatter plot of JTE composition at different reaction times from six replicate reactions**

It was observed that the replicates showed excellent similarities in product development. It was indicated 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 was confirmed that the transesterification experiments were repeatable.All the remaining 14 experiments were performed twice to check if they were repeatable. The percentage error for each was found to be less than 3%. Thus, it was confirmed that the transesterification experiments were repeatable. This demonstrated that response surface methodology with appropriate experimental design can be effectively applied to the optimization of the process of factors in a chemical reaction. This study focused on the application of response surface methodology to the optimization of JBL synthesis conditions using a chemical catalyst. This may provide useful information regarding the development of economic and efficient processes using base-catalyzed reaction systems.

3.2. Gas Chromatography and Fourier transform infrared (FTIR) analysis of the JBL

GC chromatogram of TMP ester of JBL is shown in Figure 13a. The peaks were identified and labeled based on the number of alkyl carbon groups that attached to TMP backbone. The esters formed (monoester, diester and triester) are identified by making comparisons with standard [(using the standard of triglyceride (TG), diglycerides (DG) and monoglyceride (MG) (Morgenstern et al,2006; Plattner et al, 1976; Yunus et al, 2002; Menkiti et al, 2015; Ocholi et al, 2017)].

The GC chromatogram of JBL after 6 h reaction is shown in Figures 13a. It can be seen from the chromatogram that the transesterification reaction between FAME and TMP have produced TMP esters with great conversion of diester to trimester (86.90% triester yield, Figure 13a). There was only insignificant amount (0.58%, Figure 13a) of monoester that was not converted to diester which was in turn converted to triester. However, there was still a reasonable amount of FAME in the product. This was due to the excess FAME used in the transesterification reaction. The unreacted FAME can be separated from the product by the use of high-performance liquid chromatography (HPLC) based on differences in polarity (Jieyu, 2012).Ester group of the JBL was confirmed by FTIR spectrum (Figure 13b) which showed discernable peaks between 4000 and 700 $cm^{-1}$.

The peaks located at 1228.3599 $cm^{-1}$ and 1171.4302 $cm^{-1}$which corresponds to the C – O stretching, indicate the presence of esters. The band at 1737.808 $cm^{-1}$ was for C = O stretching, usually present in the esters indicating the formation of trimethylolpropane ester. Another evidence of trimethylolpropane ester produced was the appearance of C-O-C stretching vibration peak of trimethylolpropane ester at 1171.43 $cm^{-1}$. The peak at 2890.222 $cm^{-1}$ (C – H stretching and $CH_2$ stretching) indicated the presence of carbohydrate and nucleic acids. (Menkiti et al, 2015, Barbara, 2004; Ocholi et al, 2017).

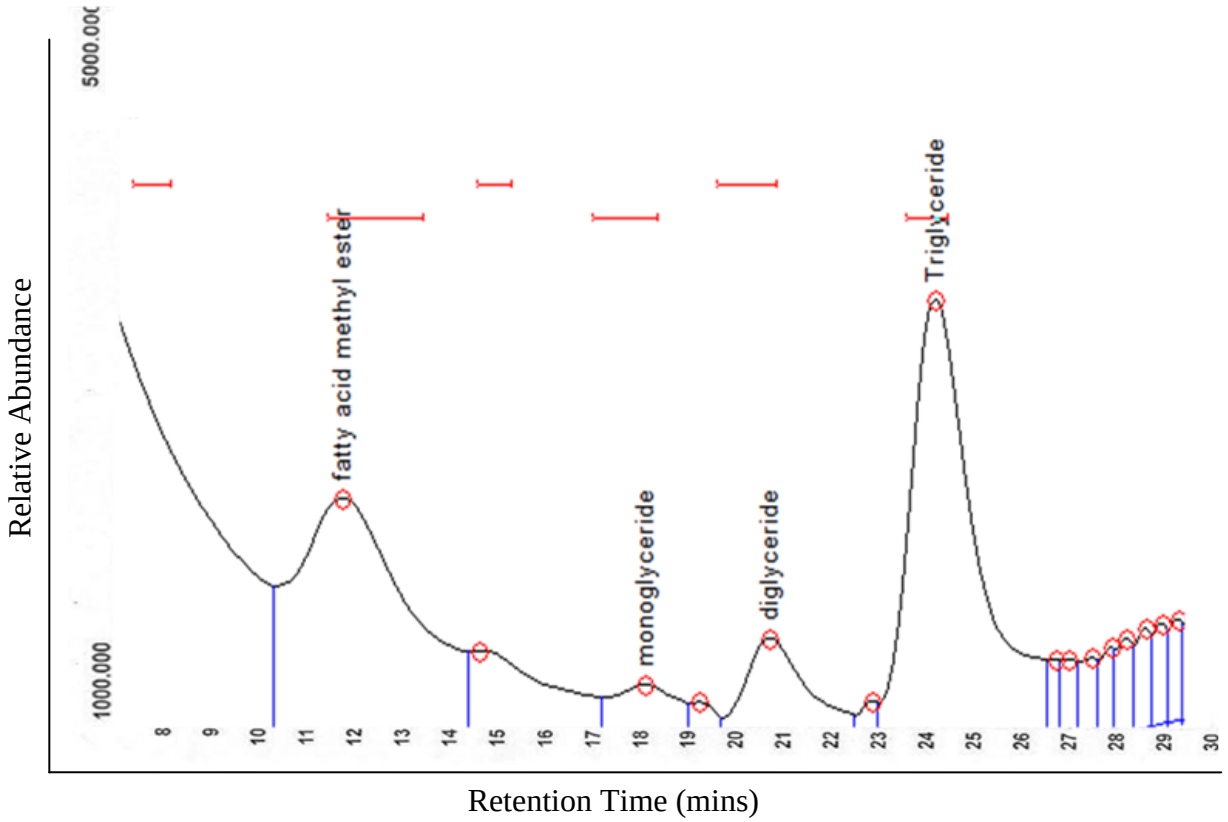


**Figure 13a: GC chromatogram of TMP ester (JBL)**

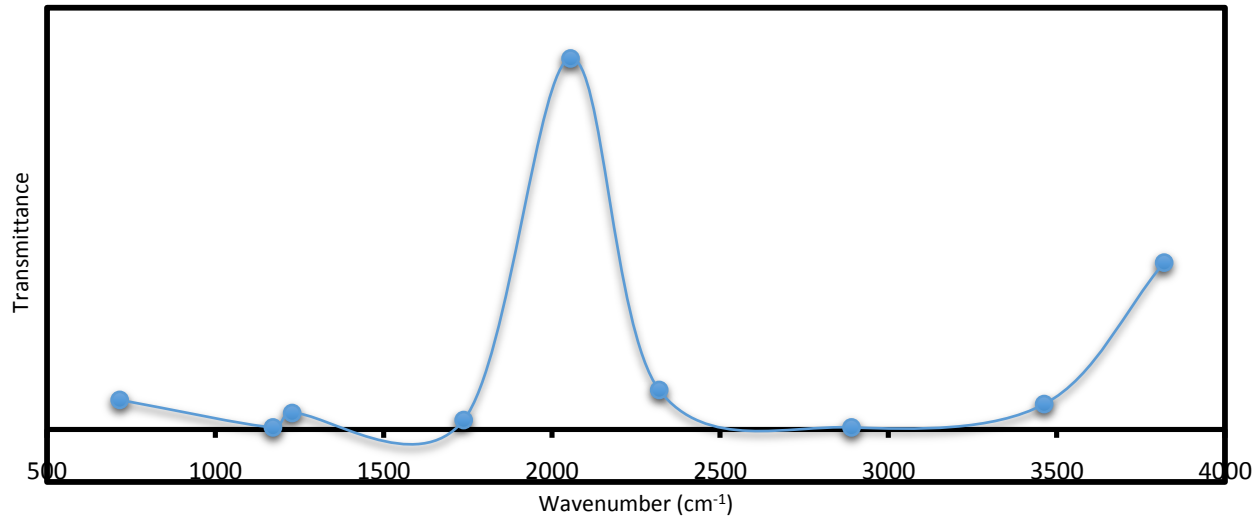


**Figure 13b:FTIR spectrum of Jatropha TMP ester**

3.3. Lubricating properties of Jatrophabiolubricant

The basic functions of a lubricant are friction and wear reduction, heat removal and contaminant suspension. Apart from important application in internal combustion engines, vehicles and industrial gearboxes, compressors, turbines or hydraulic systems, there are vast numbers of other applications, which mostly require specifically tailored

lubricants. The physicochemical and performance requirements define a lubricant identity and its ability to perform these functions. The basic properties of JBL are shown in Table 7.

**Table 7:Properties of JBL (at 140$^{o}$C, 4:1 JME-TMP mole ratio) [a]**

| Property | Units | JBL | CJO | Method |
|---|---|---|---|---|
| KV @ 40$^{o}$C | cSt | 39.45 | 17.15 | ASTM D 445 |
| KV @ 100$^{o}$C | cSt | 8.51 | 4.83 | ASTM D 445 |
| Viscosity Index (VI) | - | 204 | 233 | ASTM D 2270 |
| Pour Point (PP) | $^{o}$C | -12 | -7 | ASTM D 97 |
| Flash Point | $^{o}$C | 178 | 92 | ASTM D 93 |

[a]Menkiti et al 2017

As the most important property of a lubricant, the viscosity is the fluid's ability to resist motion. Kinematic viscosities (KV) for lubricant are usually determined at 40 and 100 $^{o}$C. JBL was found to have kinematic viscosities of 39.45 and 8.51 cSt at 40 and 100$^{o}$C, respectively. In an earlier work KV of 35.55 and 7.66 cSt were reported at 40 and 100$^{o}$C, respectively for sesame oil-based trimethylolpropane ester (Menkiti et al, 2015). Similarly, 35.43 and 7.93 cSt KV were reported for Sesame oil TMP ester (Dodos et al, 2011). Other researchers have reported the following kinematic viscosities at 40$^{o}$C: 39.7–54.1 cSt for TMP esters of palm and palm kernel oils (Yunus et al, 2003), 43.9 cSt for TMP esters of Jatrophacurcas oil (Mohamad et al, 2012) and 11.2–36.1 cSt for TMP esters of 10-undecenoic acid (Padmaja et al, 2012). The following kinematic viscosities at 100$^{o}$C were reported: 7.7–9.8 cSt (Yunus et al, 2003), 8.7 cSt (Mohd. Ghazi et al, 2009) and 3.2–7.3 cSt (Padmaja et al, 2012). These reports show a good comparison between JBL and other seed oil-based lubricant. Ideal oil for most purposes maintains a constant viscosity throughout temperature changes. The viscosity index (VI) of oil is a number that indicates the effect of temperature changes on the viscosity of the oil. A low VI signifies a relatively large change of viscosity with temperature changes. In other words, the oil becomes extremely thin at high temperatures and extremely thick at low temperatures. On the other hand, a high VI signifies relatively little change in viscosity over a wide temperature range. The higher the VI, the more preferable the lubricant is. Using the kinematic viscosity values at 40 and 100$^{o}$C, the viscosity index of JBL was found to be 204. Sripada, (2012) reported VI of 193 and 204 for the syntheses of biolubricant from methyl oleate and canola biodiesel, respectively. Meanwhile, Gryglewiczet al.,(2003)recorded a VI range of 209-235 for the synthesis of neopentyl glycol and trimethylolpropane esters of olive oil, rapeseed oil and lard fatty acids. Yunus et al., (2003) found that TMP esters of palm and palm kernel oils exhibited a very high VI of 167-187. Accordingly, Ghazi et al., (2009) and Rao et al., (2012), obtained VI of 180 for *jatrophacurcas*-derived TMP esters and 162-172 for polyol esters of 10-undecenoic acid, respectively. Furthermore, Åkerman et al., (2011) reported that TMP esters of $C_5$-$C_{18}$ fatty acids had VI of 80-208. When compared with the results obtained by other researchers, JBL had shown a relatively favourable VI.

Climatic condition is an important consideration when selecting lubricants. Therefore, viscosities and pour point values are important parameters needed to assess the performance of lubricants (Rudnick, 2006). Oil thickens as the temperature falls. At a certain temperature, it no longer flows by its weight. This temperature is called the pour point. The pour point depends on, e.g., the viscosity and chemical structure of the oil. Oil extracted from Jatropha seed was tested for pour point and viscosity and further compared with JBL. While that of crude Jatropha oil (CJO) was -7$^{\circ}$C, the pour point of JBL was -12$^{\circ}$C, indicating an improvement in pour point as a result of the transesterification reaction. This was due to the presence of a polyol group in the TMP and the absence of beta-hydrogen in the final product (Cermak and Isbell, 2003; Sharma et al, 2008).

Flashpoint measures the readiness of the oil to ignite momentarily in the air and is a consideration for the fire hazard of the oil. The Flashpoint of JBL showed great improvement over the CJO and thus justified the chemical modification of the oil. However, palm oil biolubricant showed much more stability than JBL due to the higher saturated molecules present in palm oil. (Yunus et al, 2003). There wasn't much difference between the viscosities of CJO and JBL. However, their Viscosity Index was found to be slightly lower than other plant-based biolubricants. Lubricants are usually identified according to their grades. The ISO viscosity classification is recommended for industrial applications. The reference temperature of 40 °C represents the operating temperature in machinery. Each subsequent Viscosity grade (VG) within the classification has approximately a 50% higher viscosity, whereas the minimum and maximum values of each grade range ±10% from the mid-point. Lubricants are usually identified by

their grades. Table 8 presents the specification of ISO viscosity grades and the properties of JBL. These specifications were earlier used by Mohammed et al (2012).

**Table 8: ISO viscosity grade requirement and properties of JBL(at 140$^{o}$C, 4:1 JME-TMP mole ratio)**

| Property | ISO VG32[a] | ISO VG46 [a] | ISO VG68 [a] | ISO VG100 [a] | JBL |
|---|---|---|---|---|---|
| Viscosity (Cst) | | | | | |
| 40$^{o}$C | >28.8 | >41.1 | >61.4 | >90 | 39.45 |
| 100$^{o}$C | >4.1 | >4.1 | >4.1 | >4.1 | 8.51 |
| Viscosity Index (VI) | >90 | >90 | >198 | >216 | 204 |
| Flash Point ($^{o}$C) | | | | | 178 |
| Pour point ($^{o}$C) | <-10 | <-10 | <-10 | <-10 | -12 |

[a](Rudnick, 2006)

## 4. Conclusion

In this study, experiments were conducted using response surface methodology to determine the optimal reaction conditions for the production of Jatropha biolubricant. Based on response surface methodology, the optimal values of the variables were as follows: reaction temperature of 150$^{o}$C, 200 min reaction time and JME-to-TMP molar ratio of 5:1. At this predicted optimum condition, the predicted JBL yield reached approximately 84.38%. Using these optimal factor values under experimental conditions in three independent replicates, an average JBL content of 82.74 ± 0.003% was achieved, and this value was well within the range predicted (84.38%) by the model. Further, the product composition was determined by gas chromatography while the ester group was confirmed by Fourier transform infra-red (FTIR) analysis. The quadratic polynomial model and ANOVA sufficiently explained the interaction between the process variables. Further, the model was examined and validated for the best fit. Comparative evaluation of physicochemical properties of resulting biolubricant revealed JBL satisfied the ISO VG 32 biolubricant standards. The optimized jatropha biolubricant production using calcium hydroxide as a catalyst could be applied in a jatropha biolubricant pilot plant.

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