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# TWO-STEP PRODUCTION OF BIODIESEL FROM CRUDE PALM OIL IN GAANDA, GOMBI LOCAL GOVERNMENT AREA OF ADAMAWA STATE, NIGERIA

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## ABSTRACT

*In this research work, two-step transesterification process was employed; the feedstock was first esterified using the following conditions; oil to alcohol molar ratio, 10:1, time of reaction, 90 min., temperature, 60 °C, and 3% ww of H<sub>2</sub>SO<sub>4</sub>; hence, reducing the level of the FFA of the feedstock from 3.451 % to 0.18 %. The resultant product was subsequently transesterified. All the experimental runs carried out were designed using central composite design (CCD) coupled with surface response methodology (RSM) software (Design-Expert 9 software (Stat-Ease Inc., USA)). The optimum conditions for the two-step transesterification process were; temperature (59°C), reaction time (67.50 min) and catalyst concentration (1.0 %) and the optimum biodiesel yield was 99.669 %. Thus, the yield obtained via two-step transesterification process surpassed the value provided by EN 14214 (96.5 %), besides, the physical properties determined were also within the limits of the ASTM D6751 and EN 14214 standard specifications.*

**KEYWORDS:** *temperature, Renewable energy, geothermal, marine, hydrogen*

## INTRODUCTION

Fossil fuels still represent over 80% of total energy supplies in the world, but the trend toward new energy sources in the future is clear due to the recent technological developments (Ayhan, 2008). The depletion of fossil fuel has reinforced the discussions on the renewable energy sources. Renewable energy sources such as biomass, hydro, wind, solar (thermal and photovoltaic), geothermal, marine, and hydrogen will play an important role in the near future. By the year 2040, approximately half of the global energy supply will come from renewable energy sources, and electricity generation from renewable energy will be more than 80% of the total global electricity supply

(Calero et al., 2014; Shahbaz et al., 2011 and Edmond, 2018).

Furthermore, renewable resources are more evenly distributed than fossil and nuclear sources and energy flow from renewable sources are more than three orders of magnitude higher than current global energy use. Today's energy system is unsustainable because of environmental, economic, and geopolitical concerns that have implications far into the future (Singh, et al, 2014). According to the International Energy Agency (IEA), scenarios developed for the USA and the EU indicate that near-term targets of up to 6% displacement of petroleum fuels with biofuels appear feasible using conventional biofuels, given

available crop-land. A 5% displacement of gasoline in the EU requires about 5% of available crop-land to produce ethanol, while in the USA 8% is required. A 5% displacement of diesel requires 13% of US crop-land, and 15% in the EU (Muthukumaran, Nguyen, & Baskaran, 2011). The objective of this study is to study two-steps production of biodiesel from crude palm oil using methanol.

**MATERIALS AND METHODS**

**Materials**

Methanol, sulphuric acid, potassium hydroxide, crude palm-oil, sodium sulphate, transesterification reactor, water bath, beakers, separating funnel, evaporation apparatus, thermometer and conical flasks.

**Two-Step Alkali-catalyzed Transesterification Reaction**

In the acid-catalyzed esterification process, the following conditions were adopted; oil to alcohol molar ratio, 10:1, time of reaction, 90min., temperature, 60°C, and 3% of H<sub>2</sub>SO<sub>4</sub>. The reaction mixture was then poured into a separating funnel to remove excess alcohol, sulfuric acid and impurities. The sample produced having free fatty acid of 0.185% was used for the alkali-catalyzed transesterification reaction. The crude palm oil has an initial free fatty acid value of 3.451%. The experimental set-up for alkali-catalyzed transesterification was the same as the one used for acid-catalyzed pretreatment process. It is worthy to mention that the experimental conditions presented in Table 1 were adopted for the two-step experimental process.

**Table 1. Process Variables for Biodiesel Production**

S/No.	Run.	Temp.°C	Time. Min.	Conc. %
1	8	55.00	54.00	0.50
2	11	63.00	45.00	0.50
3	20	55.00	90.00	0.50
4	5	63.00	90.00	0.50
5	6	55.00	45.00	1.50
6	9	63.00	45.00	1.50
7	7	55.00	90.00	1.50
8	2	63.00	90.00	1.50
9	14	55.00	67.50	1.00
10	9	63.00	67.50	1.00
11	12	59.00	45.00	1.00
12	18	59.00	90.00	1.00
13	4	59.00	67.50	0.50
14	17	59.00	67.50	1.50
15	15	59.00	67.50	1.00
16	13	59.00	67.50	1.00
17	10	59.00	67.50	1.00
18	3	59.00	67.50	1.00
19	1	59.00	67.00	1.00
20	16	59.00	67.50	1.00

**Statistical Analysis**

Experimental data (Table 1) were investigated via central composite design coupled with response surface methodology, in order to fit the following second-order polynomial equation generated by Design-Expert 9 software (Stat-Ease Inc., USA). Second-order coefficients were generated by means of regression. The response was initially fitted to the factors using multiple regressions. The quality of the fit of the model was assessed by means of the coefficients of determination and analysis of variance. The

quadratic response surface model was fitted to the following equation:

$$X = \beta_0 + \beta_1 Y_1 + \beta_2 Y_2 + \beta_3 Y_3 + \beta_{12} Y_1 Y_2 + \beta_{13} Y_1 Y_3 + \beta_{23} Y_2 Y_3 + \beta_{11} Y_1^2 + \beta_{22} Y_2^2 + \beta_{33} Y_3^2 \text{ ----Eq 1}$$

Where: X is the dependent variable; Y<sub>1</sub>, Y<sub>2</sub> and Y<sub>3</sub> are the independent variables; β<sub>0</sub> is the intercept, β<sub>1</sub>, β<sub>2</sub>, β<sub>3</sub>, are linear coefficients and β<sub>12</sub>, β<sub>13</sub> and β<sub>23</sub> are interaction coefficients, β<sub>11</sub>, β<sub>22</sub>, β<sub>33</sub> quadratic coefficients, respectively.

**Analysis of Biodiesel**

The yields of biodiesel samples were analyzed by a HP 6890 Gas Chromatogram (GC) equipped with

a Flame Ionization Detector (FID) and capillary column DB23 (60-m $\times$ 0.25-m $\times$ 0.15- $\mu$ m) according to a methodology proposed by Agilent. Normal hexane solutions of the biodiesel samples with a concentration of 100 mg/ml were injected by an auto injector at an oven temperature of 50 °C, which was then heated up to 230 °C. The injector temperature and the detector temperature were 250°C and 280 °C, respectively; helium was used as the carrier gas. Besides, other physical properties such as density, viscosity, cetane number, pour Point, moisture water content, cloud Point and flash point were determined using ASTM D6751 and EN 14214.

## RESULTS AND DISCUSSIONS

### Two-step Alkali-Catalyzed Transesterification Process

After production of low methyl ester content via one-step alkali-catalyzed transesterification process, a two-step alkali-catalyzed transesterification was employed to enhance biodiesel production. Firstly, free fatty acid (FFA) of the crude palm oil was reduced by an acid-catalyzed esterification process. The esterification process was done with the following conditions; oil to Alcohol molar ratio =10:1, volume of acid (H<sub>2</sub>SO<sub>4</sub>) =13.40, time of reaction =90min, and temperature =60°C. The application of these conditions reduced the FFA of the palm oil from its initial content of 3.451% to 0.185%, which is favorable for further transesterification process. Secondly, the pre-treated samples of crude palm oil were then transesterified using the conditions. After transesterification process was completed, the biodiesel samples produced were properly store and refined for analysis. The process of acidified water washing performed for the refining of the resultant crude biodiesel significantly reduced the impurities in the biodiesel.

### Separation and Purification of Biodiesel

The biodiesel produced was first subjected to gravitational settling overnight and the two distinct layers (biodiesel and glycerol) were separated via decantation. As earlier mentioned the distinct densities difference between biodiesel and glycerol and also the differences in their polarities where biodiesel is hydrophobic and glycerol being hydrophilic made their separation faster. The residual methanol was separated using evaporation equipment (temperature: 70°C and

time: 30min). However biodiesel still contain traces of impurities that need to be removed for the biodiesel produced to attain ASTM D6751 and EN14214. Therefore to achieve biodiesel standard specifications water washing was carefully performed.

### Biodiesel Acidified Water Washing

In the refining of crude biodiesel, acids including sulfuric acid, phosphoric acid, and hydrochloric acid are the mostly used agents. After acid use, distilled water is employed to wholly eliminate any water soluble impurity in biodiesel. Biodiesel is usually dried so as to be safely utilized on diesel engines, and be stored for long period of time (Atadashi et al., 2011). Faccini et al. (2010) used 10v/v% acidified water at a temperature of 55 °C to thoroughly wash biodiesel samples. The process of washing the biodiesel sample was performed in the same transesterification reactor at a temperature of 55 °C by means of constant stirring for 5 min. Afterward, the waste-water and biodiesel samples were estranged by means of a separatory funnel. The upper layer, consisting of refined biodiesel was then dried (Faccini et al., 2010). Furthermore, ethyl ester prepared from sunflower oil was refined using acidified water (5% of phosphoric acid). The yield of the produced ethyl esters obtained by using this purification method was 92.3% (Nakpong, 2010). For biodiesel to meet specifications designed by ASTM D6751 standard, the water content of fuel ought to be minimized to a maximum value of 0.050% volume by volume.

In this study, the biodiesel produced was separated from glycerol by allowing the samples to settle overnight. The resultant biodiesel was then purified using warm acidified water (10% H<sub>3</sub>PO<sub>4</sub>). In order to completely remove all the contaminants such as glycerol, residual alcohol, soap and catalyst etc, the biodiesel samples were thoroughly washed with distilled water. After which the biodiesel samples were transferred into a separatory funnel and set aside for 0.5 hr. The cleaned samples of biodiesel consisting of lighter colour was dried using 10% heated Na<sub>2</sub>SO<sub>4</sub>. Compared to EN 14214 standard specification (96.6%), most of the biodiesel samples after refining met the international standard specification for the yields of ester as shown in Table 2.

**Table 2: Yields of Biodiesel (Two-step transesterification)**

Run	Factor 1 A:Temp.°C	Factor 2 B: Time-min.	Factor 3 C: Cat. Conc %	Response 1 R1 % (Yield)
1	63.00	45.00	1.50	95.68
2	59.00	67.50	0.50	96.92
3	59.00	67.50	1.00	98.87
4	59.00	90.00	1.00	97.89
5	59.00	67.50	1.00	99.25
6	59.00	67.50	1.00	98.99
7	55.00	45.00	1.00	98.87
8	55.00	54.00	0.50	94.41
9	55.00	90.00	0.50	98.56
10	59.00	67.00	1.00	98.91
11	63.00	90.00	1.50	89.85
12	63.00	90.00	0.50	94.01
13	59.00	45.00	1.00	99.66
14	55.00	67.50	1.00	98.92
15	59.00	67.50	1.00	97.15
16	55.00	90.00	1.00	98.97
17	59.00	67.50	1.00	99.13
18	63.00	67.50	1.00	96.45
19	63.00	45.00	0.50	83.54
20	59.00	67.50	1.50	99.87

The statistical analysis of variance (ANOVA) was carried out using the software (Design-Expert 9 software (Stat-Ease Inc., USA) so as to evaluate the precision of the model, the fitness and the significance of the model, the effects of the individual parameters and interaction effects on the response. In accordance with the results obtained using the ANOVA (Table 3), the model was significant with a p-value less than 0.0001. Additionally, the Model F-value of 9.01 implies that the model is significant. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In addition, reaction temperature, A, time, B, catalyst concentration, C, reaction temperature–catalyst concentration interaction, AC, and the interaction term of reaction time–catalyst concentration, BC, were significant model terms with p-values less than 0.05 ( both the model and term p-value<0.05 indicated that the model is significant for 95% confidence intervals). Further, temperature-time interaction, AB, quadratic term of temperature, A<sup>2</sup>, quadratic term of time, B<sup>2</sup>, and quadratic term of catalyst concentration were insignificant terms (term p-

value>0.100 indicated that the model terms are insignificant). In Addition, the insignificant terms in this optimization study, were kept to improve the model precision (Montgomery, 1997; Zabeti, Daud, & Aroua, 2010).

The lack of fit is regarded as the weighted sum of squared deviations between the mean response at each factor level and the corresponding fitted value (Montgomery, 1997). In this research work the lack of fit is not significant for the response with a P-value of 0.0610 (lack of fit p-value>0.05); this indicates that the model is fitted to all data (Not-significant, lack of fit is good). Adequate precision is a measure of signal to noise ratio; it compares the range of the predicted values at the design points to the average prediction error and as prerequisite of the model, a ratio of greater than 4 is desirable. In this model, the ratio of 13.058 indicates sufficient model discrimination.

**Table 3: ANOVA for response surface quadratic model analysis of variance**

Source	Sum of Squares	Df	Mean Square	F. Value	p-value Prob-F
Model	2223.81	9	24.87	9.01	0.0010 significant
A-Temp.	21.21	1	21.21	7.68	0.0197
B-Time	14.18	1	14.18	5.14	0.0469
C-Cat. Conc.	21.47	1	21.47	7.78	0.0192
AB	7.80	1	7.80	2.82	0.1238
AC	14.26	1	14.26	5.16	0.0464
BC	16.54	1	16.54	5.99	0.0344
A	10.27	1	10.27	3.72	0.0826
B <sup>2</sup>	0.89	1	0.89	0.32	0.05825
C <sup>2</sup>	4.04	1	4.04	1.46	0.2543
Residual	27.61	10	2.76		
Lack of Fit	24.61	6	4.10	5.47	0.0034 Not Signif.
Pure Error	3.00	4	0.75		
Cor Total	251.42	19			

The quadratic model was selected as suggested by the software for biodiesel yield as shown in Table 3. The final empirical model in terms of coded factor (R1) is

shown in Eq.1. Where the values of A, B and C are in terms of coded factor represent reaction temperature, reaction time and catalyst concentration, respectively.

**Table 4 Sequential Model Sum of Squares [Type I]**

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Mean vs Total	1.891E+005	1	1.891E+005		
Linear vs Mean	130.89	3	43.63	5.79	0.0071
2FI vs Linear	43.41	3	14.47	2.44	0.1110
Quadratic vs 2FI	49.51	3	16.50	5.98	0.0133 Suggested
Cubic vs Quadratic	24.61	6	4.10	5.47	0.0610 Aliased
Residual	3.00	4	0.75		
Total	1.894E+005	20	9469.16		

**Final Equation in Terms of Coded Factors**

$$R_1 = 98.44 + 1.31 * B + 1.56 * C + 0.62 * AB + 0.59 * AC - 0.51 * BC - 1.46 * A^2 - 0.26 * B^2 - 0.30 * C^2 \text{-----Eq.1}$$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels of the factors are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

**Final Equation in Terms of Actual Factors**

The ANOVA for the response surface quadratic model is provided in Table 4. The coefficients of the response surface model as provided by Eq.2 were also evaluated. A p-value showed that all

$$R_1 = +12.07253 * \text{Temperature} - 0.32560 * \text{Time} - 16.08280 * \text{Cat. Conc.} + 0.011726 * \text{Time} + 0.67910 * \text{Temperature} * \text{cat. Conc} - 0.13664 * \text{Time} * \text{cat. Conc} - 0.11900 * \text{Temperature}^2 - 1.13865E003 * \text{Time}^2 - 4.77600 * \text{cat. Conc}^2 \text{-----Eq.2}$$

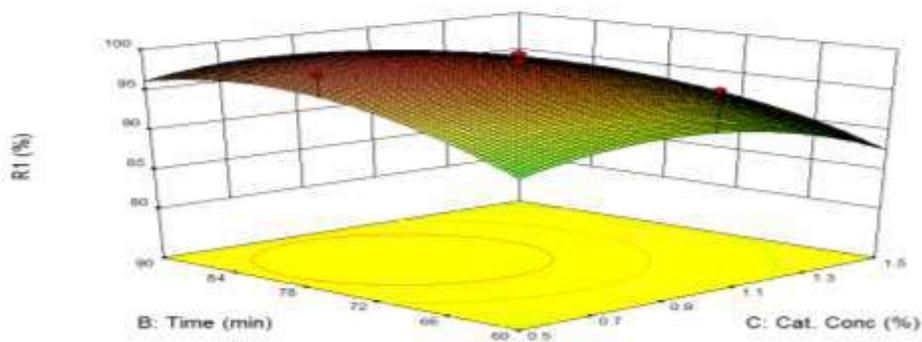
The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. It is worthy to mention that the negative sign indicates antagonistic effect while positive sign in front of the terms indicates synergistic effect. The quality of the model developed was evaluated based on the correlation coefficient value (Montgomery, 1997). The R<sup>2</sup> value was 0.9902. This signified that 99.02% of the total variation in the biodiesel yield was attributed to the experimental parameters studied. The closer the R<sup>2</sup> value to unity, the better the model will be as it will give predicted

of the linear coefficients were more highly significant than their quadratic and cross-product terms. However, in order to minimize error, all of the coefficients were considered in the design. According to the ANOVA analysis of factors, a reasonable lack of fit was noted. This indicated that the model represented the actual relationships of reaction parameters, which are well within the selected ranges (Table 4). The final estimative response model equation (based on the actual value) by which the production of biodiesel from crude palm oil was estimated was as follows:

values which are closer to the actual values for the response. The R<sup>2</sup> of 0.9902 was considered relatively high, indicating that there was a good agreement between the experimental and the predicted yield of biodiesel from this model.

**Correlation between predicted and actual**

The Figure 1 for the two-step alkali-catalyzed transesterification reaction showed that the model was able to successfully and adequately capture the correlation between the process parameters and the response (%R).



**Figures 1(a): Plots (3D) for Response surface presenting the effects of time (min) and cat. Conc (%), on the yield of biodiesel.**

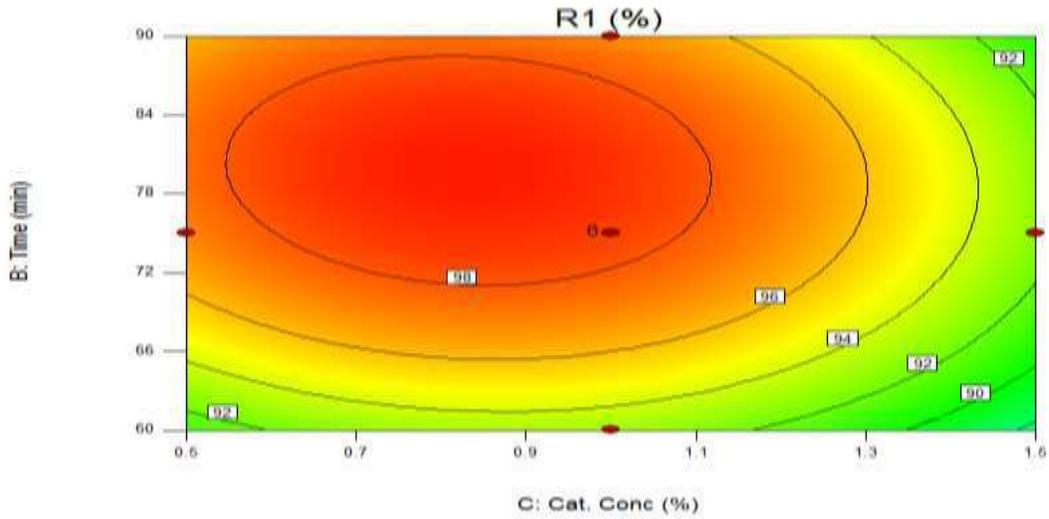


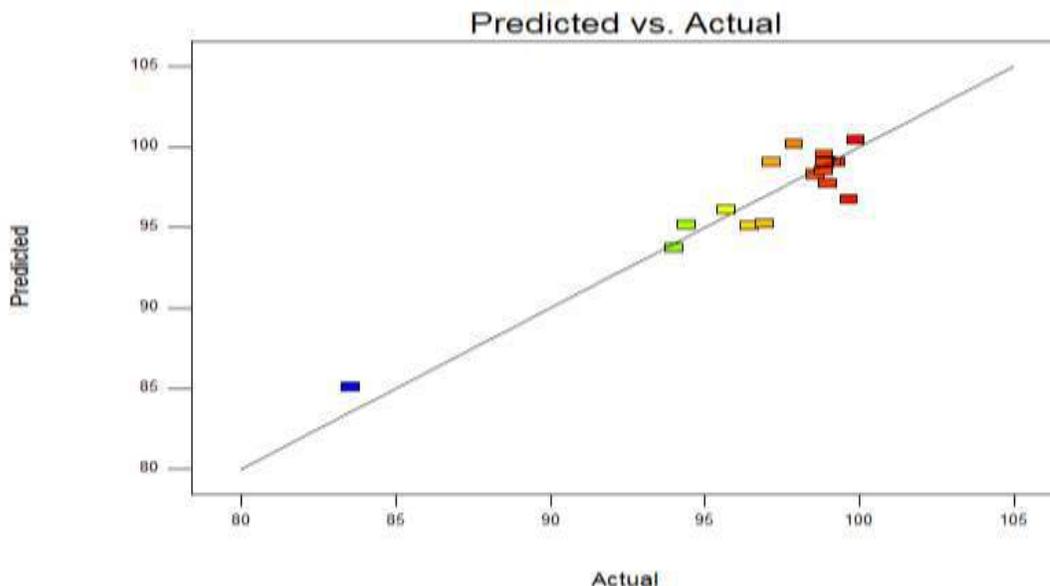
Figure 1(b): Plots (2D) for contour presenting the effects of time (min) and cat. Conc (%) on the yields of biodiesel

Table 5: Regression coefficients and significance of responsesurface quadratic model

Factor	Coefficient Estimate	df	Standard Error	95% CI		VIF
				Low	High	
Intercept	91.67	1	0.45	90.67	92.66	
A-Temperature	-2.00	1	0.42	-2.93	-1.08	1.61
B-Time	0.078	1	0.41	-0.84	0.99	2.53
C-Cat. Conc	1.45	1	0.40	0.56	2.34	4.52
AB	0.78	1	0.26	0.20	1.37	1.22
AC	0.74	1	0.19	0.32	1.15	1.38
BC	0.78	1	0.15	0.44	1.11	1.62
A <sup>2</sup>	-0.96	1	0.54	-2.16	0.24	1.99
B <sup>2</sup>	0.56	1	0.32	-0.15	1.28	3.02
C <sup>2</sup>	-0.67	1	0.18	-1.06	-0.28	5.30

For the reliability of the model to be ascertained, the data achieved should be predicted with reasonable accurateness by the model in comparison to the experimental data. Figure 2 presents predicted and

experimental values for the two-step transesterification process using the developed model equations.



**Figure 2: Correlation between predicted and actual**

The Figure 2 for the two-step alkali-catalyzed transesterification reaction showed that the model was able to successfully and adequately capture the correlation between the process parameters and the response (%R).

### CONCLUSION

The objective of this study was to produce biodiesel from crude palm oil with high free fatty acids. The FFA level of the palm oil was reduced from 3.451% to 0.185% before employing alkali-catalyzed transesterification reaction. To achieve this, acid catalyst (sulphuric acid) was used in the pretreatment reactions. The concentration of acid catalyst used had effect on the reduction of the FFA level of the crude palm oil in the pretreatment reaction. Sulphuric acid with concentration of 3% is effective for reducing FFA level of the feedstock. The FFA level of the feedstock amounting 3.451 % FFA was reduced to 0.18% . High biodiesel yield was obtained after transesterification reaction with KOH. The methyl ester yield was above 97.534%. This value is far above the value stipulated by EN14214 (96.5%). The measured fuel properties of the biodiesel properties were well within ASTM D6751 and EN 14214 biodiesel standards.

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