Characterization and Optimization of Biodiesel Produced from Palm Oil Using Acidified Clay Heterogeneous Catalyst

U. Onyekwelu Ijeoma*, T. Nwabanje Jospeh and E. Onu Chijioke

Department of Chemical Engineering, NnamdiAzikiwe University, P.M.B. 5025 Awka, Anambra State, Nigeria.

Authors’ contributions

This work was carried out in collaboration among all authors. Authors UOI and TNJ designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors TNJ and EOC managed the analyses of the study. Authors EOC and UOI managed the literature searches. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AJACR/2021/v8i330192

Editor(s):
(1) Dr. Cheikh Sall, University of Thies, Senegal.

Reviewers:
(1) Kumaran Kadirgama, Universiti Malaysia Pahang, Malaysia.
(2) Moses Aderemi Olutoye, Federal University of Technology, Nigeria.

Complete Peer review History: http://www.sdiarticle4.com/review-history/67836

Received 20 February 2021
Accepted 26 April 2021
Published 04 May 2021

ABSTRACT

The objective of the present work is to synthesize and characterize the production of biodiesel from palm oil. Acid activated heterogeneous catalyst was used in the synthesis process. The clay was characterized using SEM. The effect of process variables such as reaction temperature, catalyst weight and oil to alcohol ratio were investigated. Response surface methodology (RSM) was utilized in the design of experiment and modeling of the biodiesel production process. The biodiesel was characterized and compared to standard properties of biodiesel. The result showed that H2SO4 activation increased the surface area of the clay. In the RSM modeling, the maximum biodiesel yield obtained was 82.99% at reaction time of 5 hours, temperature of 140°C, methanol to oil ratio of 10:1, and catalyst weight of 3.6 wt%. Quadratic model with correlation coefficient of 0.9657, best described the experimental data. The physio-chemical properties of the biodiesel synthesized were comparable to the properties of standard biodiesel. This study has shown that clay heterogeneous catalyst can be used to catalyst the synthesis of biodiesel from palm oil. The finding of this study is recommended for solving some of the challenges posed by the use of fossil fuel.

*Corresponding author: Email: jioke894@gmail.com;
1. INTRODUCTION

The global concern about the protection of the environment is a major challenge facing mankind in recent times. Traditional fossil fuels constitute the major bulk of the sources of environmental degradation and global warming [1]. These sources are limited and there is already concern that they are depleting at an alarming rate and may exhaust in the near future [2,3]. Besides, the production and subsequent consumption of these fossil fuels have increased the CO\textsubscript{2} concentration in the atmosphere resulting in further environmental damage [4]. Furthermore, the unstable oil market and inevitable depletion of the world’s energy supply have ignited the interest in other sources of fuel [1]. Hence, the need for alternative, effective and renewable sources of energy such as biomass, solar, wind, nuclear, etc.

Biodiesel production has received considerable attention in recent times [5]. Biodiesel, usually defined as fatty esters derivatives from animal fats and vegetable oils through a simple transesterification process, is now seen as an alternative to diesel fuel [6,7]. It has many advantages over the conventional diesel fuel. The advantages of using biodiesel fuel are renewable, better quality of exhaust gas emissions, and biodegradability. It does not contribute to a net rise in the level of carbon dioxide in the atmosphere given that all the organic carbon present is photosynthetic in origin [8]. It emits fewer particles and much less hydrocarbons when compared with the conventional diesel fuel. It boosts the economy of the rural places since most of the raw materials are obtained from the rural areas [9].

Biodiesel is produced by the transesterification of fatty acids or vegetable oils with alcohols in the presence as acids, salts, and alkalis such as potassium hydroxide or sodium hydroxide [10]. Glycerin is usually the by-product which can also be converted to other useful applications. The biodiesel can be used unblended or in most cases, blended with conventional diesel or other biofuels to suit any particular compression ignition engine [11].

Some authors have reported on the production of biodiesel from non edible oils such as rubber seed oil [12,13], soya bean oil [14], castor seed oil [15,16], Jatropha oil [17,18], wild safflower seed oil [19], okra seed oil [20], milo seed oil [21,22], among others. Different biodiesel yields were obtained using these oils. Soya bean oil gave biodiesel yield of 78.93% with commercial potassium hydroxide as the catalyst [14]. Jatropha curcas oil and ceiba pentandra oil with combined sulphuric acid and sodium hydroxide catalyst esterification and transesterification gave biodiesel yield of 96.89% and 97.05% respectively [17]. In many cases, the choice of the oil used was influenced by environmental, natural and economic factors peculiar to the region. Encouraging yield of the biodiesel reported by some authors showed the possibility of large scale and commercial production. However, in most cases, the total cost of producing the biodiesel is the major hurdle to its commercialization in comparison to petroleum-based diesel fuel.

Nigeria, as a nation, is gifted and endowed with many mineral resources and biomass, which include; crude oils, palm oil, palm kernel shell, coal, clay, rubber, kola nuts etc [23]. Palm oil is known not only for its domestic uses but also for its industrial application. Nigeria is one of the major producers of palm oil. Industrially, palm oil serves as one of the raw materials in synthesizing some products such as biofuels, lubricants, etc. [24]. Unlike fossil fuel, palm oil can be cultivated and grown in large quantity continuously. In addition, large clay deposits abound in Awka which have not utilized. The potentials of the clay have remained untapped. Most biodiesel production reported by authors have centered on using catalysts such as potassium hydroxide, sodium hydroxide, sulphuric acid, salts etc. These catalysts are relatively expensive. Therefore, utilizing clay as catalyst (and not the conventional alkalis, acids, salts, etc) in the transesterification process may likely reduce the cost of biodiesel production.

Unlike one factor at a time (OFAT) method, modeling using response surface methodology can be used to establish the optimum process parameters involved in a process. Furthermore, it is saves time and shows the interactive relationship between the input variables [25]. Furthermore, it requires few experimental runs to establish optimum result [26]. Hence, this work was aimed at using acid activated heterogeneous clay in catalyzing the synthesis of biodiesel from palm oil and using response surface modeling to establish the optimum conditions.

Keywords: Palm oil; transesterification; clay; biodiesel; methanol.
2. MATERIALS AND METHODS

2.1 Raw Material Preparation

Palm oil was obtained from a local source in Awka, Anambra State and filtered to remove impurities. Analytical grade tetraoxosulphate VI acid and methanol solutions were used. All other reagents used were of analytical grade.

2.2 Clay Preparation

Locally sourced clay from Agu Awka, Nigeria, were treated by washing with distilled water to remove suspended particles after which the washed clay samples were sun dried for 3 days then oven dried for 4 hours at 110°C and finally sieved to a particle size of (125 - 250) micron. The clay samples were calcined in a muffle furnace at 400°C - 850°C for a period of 4.5 hours. After the calcination, for the acid activation, the calcined samples were doped with 4M sulphuric acid at different mass ratio (clay: acid, 1:2 - 1:6) under the conditions of 1 hr doping time at 90°C. The doped clay samples were further calcined for 2.5 hrs at 400 °C. After this stage of pre-treatment, the clay sample was ready for the catalysis reaction of biodiesel production.

2.3 Transesterification Process

The transesterification reaction was carried out in a three-necked 250mL round bottom flask. The set up was fitted with a digital thermometer, condenser and a mechanical stirrer.

A mixture of methanol and the clay catalyst (3.5wt% cat. to one mole of methanol) stirring at 500 rpm was allowed to react at a temperature of 100°C for 15 minutes. At the end of this period, a specific amount of the oil was introduced into the reacting mixture. The reaction was allowed to proceed until the end of 3 hours, after which the reaction was quenched. The product mixture comprising solid catalyst and the biodiesel were transferred to a separating funnel where warm water was used to quench the reaction. The reaction was then allowed to settle. Glycerol and clay being heavier than biodiesel settled at the bottom of the funnel and was drained off [27].

2.4 Effect of Process Variables on the Transesterification Experiment

The three major process parameters that affect the transesterification process are the reaction temperature, the methanol to oil ratio and the weight of catalyst loading. Batch studies were carried out to determine the effect of the process parameters. Different temperatures of 80°C, 90°C, 100°C, 120°C, 130°C; methanol to oil molar ratios of 6:1, 9:1, 12:1, 15:1; catalyst loading: 1.5wt%, 2.5wt%, 3.5wt%, 4.5wt% and 6wt% were studied for reaction times of 1, 2, 4, 5, 6 and 8 hours.

2.5 Physiochemical Properties

The cloud point and pour point were determined according to ASTM D6751 using the Kehler Model K-16270 apparatus. Viscosity was determined using Digital Viscometer SVM 3000 (Anton Paar) at 40°C temperatures according to the ASTM D-445. The density was determined using a density bottle. The flash point was determined by an automated Pensky-Martens closed-cup apparatus in the temperature range of 60 to 190°C according to ASTM D93 - 11 Standard Test Methods for flash point. Acid value was calculated by using the formula 2 x FFA% [28].

2.6 Response Surface Modeling

Design Expert Software was used in the response surface methodology. Central composite (CCD) design, being a five-level design that incorporates the axial points in the design, was used in the design of experiment and analysis of the result. Its designs provide high quality predictions over the entire design space because it generates new extremes for all factors outside the design bracket. The independent input variables were reaction time (hours), reaction temperature (°C), methanol to oil ratio and catalyst weight (wt %). These independent variables were varied at five different levels. The response was the biodiesel yield (%). The coded values of the process parameters were determined by the equation given in equation 1 [29].

\[ N_i = \frac{x_i-x_0}{\Delta x} \]  \hspace{1cm} (1)

where \( N_i \) is the coded value of the ith variable, \( x_i \) is the real value of the ith test variable, \( x_0 \) is the real value of the ith test variable at the center point, \( \Delta x \) is the step change of the variable. The summary of the 5-level factor design used in this work is shown on Table 1.

The total number of experimental runs \( N \) in CCD is given by equation 2 [26].

\[ N = 2^n + 2n + n_c \]  \hspace{1cm} (2)

Where \( n \) is the number of independent factors or input variables and \( n_c \) is the number of center
points or null points chosen. The term $2^n$ corresponds to the core (factorial) points, $2n$ corresponds to the star-like or axial points and $n_c$ corresponds to the center points. Therefore, by using six (6) center points, a total of thirty (30) experimental runs were utilized in the CCD process. This consists of 16 core points, 8 star-like points and 6 center points. The experiments were performed in random in order to avoid systematic error.

3. RESULTS AND DISCUSSION

3.1 Scanning Electron Micrograph

The SEM images for the raw and calcined Agu-Awka clay samples were shown in Figs. 1 and 2 respectively.

From the morphological features of the raw clay sample, it could be seen that the clay particles were composed of individual lamellae and reduced particle cohesion. Comparing the particle distribution plot for both raw and calcined samples, it could be seen that the calcined samples contain a higher concentration of particles with larger surface area than the raw sample. The improved surface area observed in the calcined clay is as a result of the calcination process which facilitated the reduction of volatile matter thus increasing the surface area of the sample.

3.2 Properties of the Oil

Some of properties of the oil are given in Table 2. The oil has high viscosity and free fatty acid which will hinder their direct use as fuel in diesel engines. Their high viscosity can have negative impact in the atomization of the fuel spray and function of the fuel injectors. The acid value was found to be 1.315 mgKOH/g, which corresponded to a free fatty acid value of 0.661%. Saponification value of 182.3 mgKOH/g oil was obtained for the oil.

3.3 Effect of Process Variables

3.3.1 Effect of calcination temperature and doping ratio on yield of biodiesel

The effect of clay catalyst calcination temperature and doping ratio on the yield of the biodiesel was given in Fig. 3. It was seen that there was a gradual increment in the yield of biodiesel as the calcination temperature was increased from 400°C to 650°C. At 650°C the clay catalyst recorded the highest activity rate for all for the doping ratios. Beyond this temperature, there was a decrease which is because of decomposition of active catalyst sites by high temperature, therefore the best calcination temperature for the activation of the clay for biodiesel production at 150minutes is 650°C.

Table 1. Factor levels used in the design of experiment

| Parameter       | Symbol | Unit | -α   | Low   | Medium | High   | +α   |
|-----------------|--------|------|------|-------|--------|--------|------|
| Temperature     | $X_1$  | °C   | 60   | 75    | 100    | 125    | 140  |
| Reaction time   | $X_2$  | hrs  | 1.96 | 3.1   | 5.0    | 6.9    | 8.04 |
| Molar ratio     | $X_3$  |      | 5.2  | 7.0   | 10.0   | 13.0   | 14.8 |
| Cat. Wt.        | $X_4$  | %    | 1.2  | 2.1   | 3.6    | 5.1    | 6    |

Fig. 1. SEM image of the raw clay at magnification of 500x
Table 2. Physical and chemical properties of oil feedstock

| Properties                  | Palm Oil     |
|-----------------------------|--------------|
| Acid value (A.V), mg KOH/g  | 1.315        |
| Free fatty acid (FFA), %    | 0.661        |
| Saponification value, mg KOH/g | 182.3     |
| Iodine value, g/100g        | 118.35       |
| Pour point, °C              | 12.5         |
| Cloud point, °C             | 16           |
| Density, g/cm³              | 0.901        |
| Viscosity, cP               | 20.5         |

Furthermore, it was seen that the optimum activation ratio was 1:5 w/w. Beyond the optimum point, the hydrogen ion contained in the fixed volume of solvent was not mobile enough to activate and provide reaction sites in the clay mineral. This is due to the clogging of the hydrogen ions as a result of the increased concentration of the acid relative to the clay.

**3.3.2 Effect of reaction temperature on yield of biodiesel**

The effect of reaction temperature on the yield of biodiesel was shown on Fig. 4. It was seen that there was accelerated yield of biodiesel at all temperature levels within the first 240 minutes of reaction. The yield of biodiesel increased steadily from 60°C to 120°C. The normal behavior for catalyzed reaction is that the yield rate increase with temperature. The higher the temperature the shorter the time to reach the maximum yield, thus transesterification is an endothermic reaction. The biodiesel yield increased with increasing reaction temperature and maximum yield of 83.7% was obtained at 100°C. However, at temperature above 100°C, the biodiesel yield decreases. The vaporization of methanol is too high and it remains on the reactor, thus results in a decrease in the amount of methanol available for reaction. Moreover, the polarity of methanol also decreased at high temperature leading to a decrease in the concentration of reactive methoxides species in the mixture. Siddalingappa and Omprakash [30] reported maximum biodiesel yield at temperature of 70°C from sugar apple seed oil using sodium hydroxide catalyst.

**3.3.3 Effect of clay catalyst weight on yield of biodiesel**

The plots of the biodiesel yield as a function of clay heterogeneous catalyst loading was presented on Fig. 5. It can be seen that the reaction rate increased with increase in clay catalyst loading from 1.5w/w% to a maximum 3.5w%. The increase in conversion as the amount of catalyst is increased indicated that the availability of active site for the transesterification reaction increased. Increasing the catalyst weight further
beyond 3.5wt % led to a sharp decrease in the yield of biodiesel. Addition of an excessive amount of catalyst gives rise to the formation of an emulsion which increases the viscosity of the mixture and leads to the formation of gels, hence declining the conversion of the oil to biodiesel [31].

**Fig. 3.** Effect of calcination temperature and catalyst doping ratio on yield of biodiesel (at transesterification temperature of 120 °C, catalyst weight of 3.5 wt% and oil to alcohol ratio of 15:1)

**Fig. 4.** Effect of reaction temperature on yield of biodiesel (at catalyst weight of 3.5 wt% and oil to alcohol ratio of 15:1)
3.3.4 Effect of oil to alcohol molar ratio on yield of biodiesel

The effect of molar ratio was studied across five different levels of molar ratio (6:1, 9:1, 12:1, 15:1 and 18:1) at a temperature of 120°C and a catalyst loading of 3.5wt% as shown in Fig. 6. The conversion increased with increase in molar ratio from 6:1 to 15:1. The conversion above 15:1 molar ratio produced a reduction in the yield of biodiesel. At low ratio of methanol to oil, the reacting solution forms a poor suspension and poor miscibility or solubility of methanol in the oil resulting into low biodiesel yield. The reduction can also be as a result of deactivation of the catalyst by excessive amount of methanol [32,33].

3.5 RSM Modeling of the Transesterification Process

The responses obtained from combination of the four process variables in different experimental runs were tabulated in Table 3. The four-experimental variable interaction gave a total of 30 experimental runs comprising of 24 distinct runs and 6 similar repeated runs usually called the centre points. The responses obtained from various runs are significantly exceptional which implies that each of the factors have substantial effect on the response. The maximum biodiesel yield obtained was 82.99% at reaction time of 5 hours, temperature of 140°C, methanol to oil ratio of 10:1, and catalyst weight of 3.6 wt%.

The model summary statistics table in Table 4 showed that quadratic model was suggested as the best model. The cubic model was aliased. The R-squared, predicted R-squared, and adjusted R-squared values for the quadratic models show a high value of 0.9657, 0.8937, and 0.9336 respectively.

The measure of how efficient the variability in the actual response values can be explained by the experimental variables and their interactions is given by the R-Squared value. The higher the R$^2$ value, the better the model predicts the response. The predicted-R$^2$ and the adjusted-R$^2$ should be within 0.20 of each other. Otherwise there may be a problem with either the data or the model [34]. Furthermore, the quadratic model has the lowest standard deviation value of 3.33.

3.5.1 ANOVA analysis and model fitting

The ANOVA and model fitting analysis were presented in Table 5. The adequacy of the models was evaluated by applying the lack-of-fit test. This test is used in the numerator in an F-test of the null hypothesis and indicates that a proposed model fits well or not. The test for lack-of-fit compares the variation around the model with pure variation within replicated observations. This test measured the adequacy of the different models based on response surface analysis. The low f-values for lack of fit depict its insignificance relative to pure error. Non-significant lack of fit is
good because it means the model will be well fitted. The significance of the model and each coefficient was determined using the F-test and p-value. The corresponding variables would be more significant if the absolute F-value becomes greater and the p-value becomes smaller [35,36]. The quadratic model was seen as the best model for the transesterification process.

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The coefficient of variation (CV) is defined as the ratio of the standard deviation of estimate to the mean value of the observed responses. The result of the CV obtained was below 10% indicating that the quadratic model can reasonably reproduce the output of the transesterification process [29,37]. The signal to noise ratio which is given as the value of the adequacy precision indicates that an adequate relationship of signal to noise exists. An adequate precision ratio value greater than 4 indicates adequate model efficacy [38]. The results showed that the adequate precision ratio was 19.23. This was well above the recommended minimum of 4, hence good model efficacy is implied of the chosen quadratic model [39,40].

Based on these results, the effect of each parameter and the combined effects of parameters were evaluated using quadratic model in equation 3.

Biodiesel yield (%) = +71.42 + 10.96A + 2.02B + 3.53C + 0.61D + 1.27AB + 4.33AC + 1.59AD – 3.55BC – 0.24BD – 3.20CD – 2.33A² – 4.05B² – 5.79C² – 2.62D² 

(3)

The quadratic model indicated that most of the independent variables have positive effect on the biodiesel yield. This is because positive sign in front of these factors shows that the percentage moisture content is favoured by increase in such a factor, while negative sign represents decrease in such factors [41].

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. The response values obtained by inserting the independent values in the quadratic mode equation were the predicted values of the model. These values were compared to the experimental values in Table 3.

From the ANOVA table, model terms D, AB, AD, and BD are insignificant. Expunging the insignificant terms will lead to reduced and improved model with relatively small number of terms. Therefore, the improved model equation after eliminating the insignificant terms will be as given in equation 4.

Biodiesel yield (%) = +71.42 + 10.96A + 2.02B + 3.53C + 4.33AC – 3.55BC – 3.20CD – 2.33A² – 4.05B² – 5.79C² – 2.62D² 

(4)
### Table 3. Result of design of experiment

| Run No | Temp (°C) | Time (hrs) | Methanol to oil ratio | Catalyst weight (wt%) | Experimental biodiesel yield (%) | Predicted biodiesel yield (%) |
|--------|-----------|------------|-----------------------|-----------------------|---------------------------------|-------------------------------|
| 1      | 100       | 5          | 10                    | 3.6                   | 71.54                           | 71.42                         |
| 2      | 100       | 8.04       | 10                    | 3.6                   | 65.23                           | 64.29                         |
| 3      | 125       | 3.1        | 13                    | 5.1                   | 77.33                           | 74.97                         |
| 4      | 100       | 5          | 14.8                  | 3.6                   | 60.9                            | 62.25                         |
| 5      | 100       | 5          | 10                    | 3.6                   | 69.93                           | 71.42                         |
| 6      | 100       | 5          | 5.2                   | 3.6                   | 50.44                           | 50.95                         |
| 7      | 125       | 3.1        | 7                     | 2.1                   | 46.84                           | 47.26                         |
| 8      | 100       | 5          | 10                    | 3.6                   | 68.72                           | 71.42                         |
| 9      | 100       | 1.96       | 10                    | 3.6                   | 55.03                           | 57.84                         |
| 10     | 100       | 5          | 10                    | 6                     | 65.48                           | 65.69                         |
| 11     | 125       | 6.9        | 7                     | 2.1                   | 62.63                           | 61.40                         |
| 12     | 125       | 3.1        | 13                    | 2.1                   | 76.59                           | 76.48                         |
| 13     | 100       | 5          | 10                    | 3.6                   | 80.94                           | 71.42                         |
| 14     | 75        | 3.1        | 7                     | 2.1                   | 40.28                           | 39.72                         |
| 15     | 75        | 3.1        | 13                    | 5.1                   | 41.29                           | 43.75                         |
| 16     | 100       | 5          | 10                    | 1.2                   | 62.07                           | 63.72                         |
| 17     | 75        | 6.9        | 13                    | 5.1                   | 40.5                            | 37.67                         |
| 18     | 125       | 6.9        | 7                     | 5.1                   | 71.13                           | 71.72                         |
| 19     | 75        | 6.9        | 13                    | 2.1                   | 45.37                           | 46.49                         |
| 20     | 125       | 3.1        | 7                     | 5.1                   | 58.43                           | 58.54                         |
| 21     | 100       | 5          | 10                    | 3.6                   | 68.82                           | 71.42                         |
| 22     | 100       | 5          | 10                    | 3.6                   | 71.26                           | 71.42                         |
| 23     | 140       | 5          | 10                    | 3.6                   | 82.99                           | 82.99                         |
| 24     | 75        | 3.1        | 7                     | 5.1                   | 46.96                           | 44.65                         |
| 25     | 60        | 5          | 10                    | 3.6                   | 46.08                           | 47.94                         |
| 26     | 75        | 6.9        | 7                     | 5.1                   | 51.43                           | 52.77                         |
| 27     | 125       | 6.9        | 13                   | 5.1                   | 72.16                           | 73.95                         |
| 28     | 125       | 6.9        | 13                   | 2.1                   | 76.53                           | 76.42                         |
| 29     | 75        | 3.1        | 13                   | 2.1                   | 54.62                           | 51.61                         |
| 30     | 75        | 6.9        | 7                     | 2.1                   | 48.85                           | 48.80                         |
Table 4. Model summary statistics

| Source  | Dev. | R-Squared | Adjusted R-Squared | Predicted R-Squared | PRESS  |
|---------|------|-----------|--------------------|---------------------|--------|
| Linear  | 8.86 | 0.5959    | 0.5312             | 0.4348              | 2743.6 |
| 2FI     | 8.04 | 0.7468    | 0.6135             | 0.3980              | 2922   |
| Quadratic | 3.33 | 0.9657    | 0.9336             | 0.8937              | 515.9  |
| Suggested |     |           |                    |                     |        |
| Cubic   | 4.29 | 0.9735    | 0.8903             | 0.2084              | 3842.3 |

Table 5. ANOVA table

| Source            | Sum of Squares | Df | Mean Square | F Value | p-value | Prob > F |
|-------------------|----------------|----|-------------|---------|---------|----------|
| Model             | 4687.4         | 14 | 334.81      | 30.13   | <0.0001 |          |
| A-Temperature     | 2535.2         | 1  | 2535.23     | 228.12  | <0.0001 |          |
| B-Reaction time   | 85.84          | 1  | 85.84       | 7.72    | 0.0140  |          |
| C-Molar ratio     | 263.33         | 1  | 263.33      | 23.69   | 0.0002  |          |
| D-Cat. Wt.       | 7.97           | 1  | 7.97        | 0.72    | 0.4103  |          |
| AB                | 25.65          | 1  | 25.65       | 2.31    | 0.1495  |          |
| AC                | 300.33         | 1  | 300.33      | 27.02   | 0.0001  |          |
| AD                | 40.32          | 1  | 40.32       | 3.62    | 0.0762  |          |
| BC                | 201.64         | 1  | 201.64      | 18.14   | 0.0007  |          |
| BD                | 0.92           | 1  | 0.92        | 0.082   | 0.7773  |          |
| CD                | 163.71         | 1  | 163.71      | 14.7    | 0.0016  |          |
| A^2               | 75.79          | 1  | 75.79       | 6.82    | 0.0196  |          |
| B^2               | 229.39         | 1  | 229.39      | 20.64   | 0.0004  |          |
| C^2               | 469.40         | 1  | 469.40      | 42.24   | <0.0001 |          |
| D^2               | 96.37          | 1  | 96.37       | 8.67    | 0.0100  |          |
| Residual          | 166.70         | 15 | 11.11       |         |         |          |
| Lack of Fit       | 60.97          | 10 | 6.09        | 0.29    | 0.9554  |          |
| Pure Error        | 105.73         | 5  | 21.15       |         |         |          |
| Cor Total         | 4854.1         | 29 |             |         |         |          |
| Coefficient of variance (CV) | 5.46 | | | | |
| Adequate precision| 19.23          |    |             |         |         |          |
The perturbation plot and the plot of predicted against actual values were given in Figs. 7 and 8, respectively. The perturbation plot showed the deviation of the independent variables from the reference point, that is, the mean. The predicted against actual plot showed that the experimental values were distributed confidently near the predicted values, implying a good correlation between the actual and predicted values. This relationship is desirable for optimization step because the predicted optimal result will have an insignificant deviation from the experimental value. The points of the normal distributions are seen to be mostly interlocked with the straight line with a few points lying outside the diagonal line in a moderately scattered manner.

### 3.5.2 3-D surface and interaction plots

In order to visualize the relationship between the experimental variables and the response, and to study individual and interaction effects of the four factors consisting of the reaction temperature, the reaction time, catalyst weight, and molar ratio of ethanol to oil, response surfaces and interaction plots were generated from the quadratic model, as shown in Figs 9 to 11. These figures illustrate the response of different experimental variables and can be used to identify the major interactions between the variables.
Fig. 9. 3D plot showing the interactive effects of reaction time and temperature

Fig. 10. 3D plot showing the interactive effects of molar ratio and reaction time

Fig. 11. 3D plot showing the interactive effects of catalyst weight and molar ratio
Table 6. Physico-chemical properties of the biodiesel and standard

| Properties          | ASTM D6571 standard | Produced Biodiesel |
|---------------------|----------------------|-------------------|
| Density (g/cm³)     | 0.86 – 0.89          | 0.87              |
| Viscosity (cP)      | 1.9 – 6.0            | 3.5               |
| Cloud point (°C)    | -3 – 15              | 4.5               |
| Pour point (°C)     | -5 – 10              | 6                 |
| Cetane number       | Min 47               | 49                |
| Flash point (°C)    | Min 130              | 181               |
| Acid value (mg KOH/g)| ≤0.5                 | 0.44              |

3.6 Physio-Chemical Properties of the Biodiesel

Important fuel properties such as density, viscosity, pour point, cloud point, cetane number, and flash point of the biodiesel produced were determined and the results presented in Table 6. The results showed that the properties of biodiesel produced fell within the acceptable standard. The reduction in viscosity is very important for the efficiency of the engine. Many modern diesel engines use high technological injection pumps, which do not tolerate high viscous fluids because it clog fuel filters and become very risky to use at low surrounding temperature. Fuel atomization is also affected by viscosity. The 3.5 cP viscosity of the biodiesel obtained was within the ASTM D6571 standard of 1.9 to 6.0 cP. The acid value (AV) is a simple method for monitoring fuel quality. The AV of the biodiesel was 0.44 mg KOH/g, which satisfied the maximum AV of 0.50 mgKOH/g set in ASTM D6751 standard. The flash point was 181°C. Flash point is the lowest temperature at which fuel emits enough vapour to ignite.

4. CONCLUSION

In the present work, acid activated clay was used as catalyst to successfully synthesized biodiesel from palm oil. The effects of oil to alcohol ratio, clay catalyst weight and reaction temperature on the yield of biodiesel were examined. The activation process positively modified the clay catalyst which enhanced the transesterification process. The process variables have significant effect on the yield of biodiesel. RSM modeling showed that quadratic model best described the production process with optimum yield of biodiesel of 82.99%. The RSM predicted biodiesel yields closely tracked the experimental biodiesel yields. From the study, it was concluded that acid activated clay heterogeneous catalyst can be used in the transesterification of palm oil to synthesize biodiesel. It is recommended that further investigations be carried out using alkaline activated heterogeneous catalyst.

ACKNOWLEDGEMENT

The authors will like to acknowledge the department of Chemical Engineering, Nnamdi Azikiwe University Awka, Nigeria for the facilities provided for this research work.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Okechukwu ME, Nwabanne JT, Onu CE, Ifeanyi CEU. Kinetic study of dilute acid hydrolysis of cowpea seed husk for production of glucose. Journal of Materials Science Research and Reviews. 2019; 4(4):1-10.
2. Amadi BC, Igbokwe PK, Onu CE. Enzymatic hydrolysis of blend of lignocellulosic materials for reducing sugar production: screening of significant process factors. Asian Journal of Chemical Sciences. 2020; 8(4):1-10. DOI: 10.9734/AJOCS/2020/v8i419048
3. Alemayehu G, Amanu L. Production of biodiesel from non edible oil and its properties. International Journal of Science, Environment and Technology. 2014;3(4):1544–1562.
4. Peter W, Betina J, Lene L, Birgitte KA, Claus HC. International Journal of Hydrogen Energy. 2007;32:4135.
5. Omoloso MA, Akinsanoye OA. A review of biodiesel generation from non edible seed oils crop using non conventional heterogenous catalysts. Journal of...
Petroleum Technology and Alternative Fuels. 2015;6(1):1 – 12. DOI: 10.5897/JPTAF2014.0108
6. Amit A, Pankaj G, Rajdeep E. Biodiesel production for c.i. engine from various non-edible oils: A review. International Journal of Emerging Engineering Research and Technology. 2015;3(1):8-16.
7. Ma F, Clements LD, Hana MA. The effects of catalyst, free fatty acids and water on transesterification of beef tallow. Trans Am Soc Agric Eng. 1999;41:1261-4.
8. Aworanti OA, Agarry SE, Ajani AO. Statistical optimization process variables for biodiesel production from waste cooking oil using heterogeneous base catalyst. British Biotechnology journal. 2013;3(2):116-132.
9. Anton AK, Alexandre CD, Gadi R. Solid acid catalysts for biodiesel production—towards sustainable energy. American Oil Chemists Society. 2005;1660:4 – 7.
10. Knothe G. Biodiesel and renewable diesel: A comparison. Progress in Energy and Combustion Science. 2010;36(3):364–373.
11. Van-Gerpan JV. Biodiesel processing and production. Fuel Processing Technology. 2005;86:1097-1107.
12. Ramadhas AS, Jayaraj S, Muraleedharan C. Biodiesel production from high FFA rubber seed oil. Fuel. 2005;84(4):335–340.
13. Ikwuagwu OE, Ononogbu IC, Njoku OU. Production of biodiesel using rubber [Hevea brasiliensis (Kunth. Muell.)] seed oil. Industrial Crops and Products. 2000;12(1):57–62.
14. Nwadike EC, Abonyi MN, Onu CE, Obika EN. Synthesis and optimization of biodiesel from soya bean. International Journal of Mechanical and Production Engineering. 2019;7(12):98–105.
15. Meneghetti SMP, Meneghetti MR, Wolf CR. Ethanolysis of castor and coconut seed oil: a systematic study using classical catalysts. Journal of the American Oil Chemists' Society. 2006; 83(9):819–822.
16. Chakrabarti MH, Ahmad R. Transesterification studies on castor oil as a first step towards its use in biodiesel production. Pakistan Journal of Botany. 2008;40(3):1153–1157.
17. Ong, HC, Silitonga AS, Masjuki HH, Mahlia TMI, Chong WT, Boosroh MH. Production and comparative fuel properties of biodiesel from non-edible oils: Jatropha curcas, Sterculia foetida and Ceiba pentandra. Energy Conversion and Management. 2013; 73:245–255.
18. Nakpong P, Wootthikanokkhan S. Optimization of biodiesel production from Jatropha curcas L. oil via alkali-catalyzed methanolysis. Journal of Sustainable Energy & Environment. 2013;1(3):105–109.
19. Sadia H, Ahmad M, Zafar M, Sultana S, Azam A, Khan MA. Variables effecting the optimization of non edible wild safflower oil biodiesel using alkali catalyzed transesterification. International Journal of Green Energy. 2013;10(1):53–62.
20. Anwar F, Rashid U, Ashraf M, Nadeem M. Okra (Hibiscus esculentus) seed oil for biodiesel production. Applied Energy. 2010;87(3):779–785.
21. Panchal B, Dhoot S, Deshmukh S, Sharma M. Optimization of extraction of oil and biodiesel from Thespesia populnea seed oil by alkali-catalyst in India. International Journal of Green Energy; 2012.
22. Rashid U, Anwar F, Yunus R, Al-Muhtaseb AH. Transesterification for biodiesel production using Thespesia populnea seed oil: an optimization study. International Journal of Green Energy. 2014;12(5):479–484.
23. Nwabanne JT, Okpe EC, Igboke P, Assadu CC, Onu CE. Isotherm and kinetic modelling of adsorption of dyestuffs onto kola nut (cola acuminate) shell activated carbon. Journal of Chemical Technology and Metallurgy. 2016;51(2):188–201.
24. Nwabanne JT, Onu CE, Nwankwoukwu OC. Equilibrium, Kinetics and Thermodynamics of the Bleaching of Palm Oil Using Activated Nando Clay. Journal of Engineering Research and Reports. 2018;1(3):1–13. DOI: 10.9734/JERR/2018/42699.
25. Iheanacho CO, Nwabanne JT, Onu CE. Optimum process parameters for activated carbon production from rice husk for phenol adsorption. Current Journal of Applied Science and Technology. 2019;36(6):1-11. DOI: 10.9734/CJAST/2019/v36i630264.
26. Assadu CC, Onu CE, Nwabanne JT, Ohale PE, Assadu CO. Comparative analysis of RSM, ANN and ANFIS and the mechanistic modeling in eriochrome black-T dye adsorption using modified clay. South African Journal of Chemical Engineering. 2021;36:24–42. Available: https://doi.org/10.1016/j.sajce.2020.12.003

27. Humphrey I, Obot NI, Chendo MAC. Utilization of some non-edible oil for biodiesel production. Nigeria Journal of Pure and Applied Physics. 2017;7(1):1–6.

28. AOAC, Official methods of analysis if the analysis of the Association of Official Analytical Chemists 15th Edition. Association of Official Analytical Chemists. Washington DC; 1990.

29. Onu CE, Igbokwe PK, Nwabanne JT., Nwanjinka OC, Ohale PE. Evaluation of optimization techniques in predicting optimum moisture content reduction in drying potato slices. Artificial intelligence in Agriculture. 2020;4:39–47. Available:https://doi.org/10.1016/j.aiia.2020.04.001.

30. Siddalingappa RH, Omprakash DH. Biodiesel Production Process Optimization from Sugar Apple Seed Oil (Annona squamosa) and Its Characterization. Journal of Renewable Energy; 2015. Available:http://dx.doi.org/10.1155/2015/14857.

31. Lee JS, Saka S. Biodiesel production by heterogeneous catalysts and supercritical technologies. Bioresour Technol. 2011;101:7191—200.

32. Viriya EN, Krasae P, Nualpaeng W, Yoosuk B, Faungnawakij K. Biodiesel production over Ca-based solid catalysts derived from industrial wastes. Fuel. 2012;92:239-44.

33. Teng G, Gao L, Xiao G, Liu H. Transesterification of soybean oil to biodiesel over heterogeneous solid base catalyst. Energy Fuel. 2009;23:463.

34. Taran M, Aghaie E. Designing and optimization of separation process of iron impurities from kaolin by oxalic acid in bench-scale stirred-tank reactor. Applied clay science. 2015;107:109-116. Available:https://doi.org/10.1016/j.clay.2015.01.010.

35. Onu CE, Nwabanne JT. Application of Response Surface Methodology in Malachite green adsorption using Nteje clay. Open Journal of Chemical Engineering and Science. 2014;1(2):19 – 33.

36. Amani-Ghadim AR, Aber S, Olad A, Ashassi-Sorkhabi H. Optimization of electrocoagulation process for removal of an azo dye using response surface methodology and investigation on the occurrence of destructive side reactions. Chemica Engineering and Processing. 2013;64:68-78.

37. Chen G, Chen J, Srinivasakannan C, Peng J. Application of response surface methodology for optimization of the synthesis of synthetic rutile from titania slag. Applied Surface Science. 2011;258(7):3068–3073.

38. Okpe EC, Asadu CO, Onu CE. Statistical analysis for orange G adsorption using cola nut shell activated carbon. Journal of the Chinese Advanced Materials Society. 2018;1–9. DOI: 10.1080/22243682.2018.1534607

39. Noordin MY, Venkatesh VC, Sharif S, Elting S, Abdullah A. Application of response surface methodology in describing the performance of coated carbide tools when turning AISI 1045 steel. J. Mater. Process. Technol. 2004;145:46–58.

40. Ogugbnobi NC, Onu CE, Onukwuli OD. Adsorption of a dye (crystal violet) on an acid modified non-conventional adsorbent. Journal of Chemical Technology and Metallurgy. 2019;54(1):95-110.

41. Nwabanne JT, Okpe EC, Asadu CO, Onu CE. Application of Response Surface Methodology in Phenol Red Adsorption Using Kola Nut (Cola acuminata) Shell Activated Carbon. International Research Journal of Pure & Applied Chemistry. 2017;15(4):1–14. DOI: 10.9734/IRJPAC/2017/39421