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Optimization of Neem oil esterification using response surface methodology

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ABSTRACT

High production cost of biodiesel as well as food-versus-fuelcrisis within the economy have led to the adoption of non-edible feedstock over edible feedstock, the high FFA associated with the former remains a challenge. Esterifying high free fatty acid (FFA) oil with acid is necessary to avoid soap formation during biodiesel production. Thus, this study evaluated the efficacy of response surface methodology (RSM) in modelling the esterification process for neem seed oil (NSO) with a high FFA catalyzed by sulphuric acid H_2SO_4. A central composite design (CCD) with two level-three factors (2^3) was applied to examine the influence of Reaction time (60-120 minutes), Catalyst concentration (1.0-3.0 w/w,%), methanol to oil ratio (0.20-0.60w/w,%) and constanttemperature at 60ºC on reduction of the high FFA (4.77%) of neem. The Optimum conditions for the esterification process is 0.67 % FFA at 0.4 Methanol to Oil ratio; 90 min. Reaction Time; and 2 (w/w) % H_2SO_4Catalyst Concentration. Statistics for the RSM model showed that the correlation coefficient (R^2) value (0.9457) is relatively high, close to 1, which is desirable and is in reasonable agreement with the adjusted R^2 value (0.8969).

1. Introduction

The search for alternative fuels has intensified due to the unpredictable nature of crude oil supply, price fluctuations, political leverage, and growing environmental concerns. Alternative fuels serve as substitutes for petroleum-based fuels, meeting specific criteria like as being biodegradable, technically feasible, non-toxic, environmentally acceptable, renewable, economically competitive, and having readily available feedstocks (Helen et al., 2021). Among these options, biodiesel has emerged as a promising contender. Biodiesel is defined as the monoalkyl ester of long-chain fatty acids derived from renewable bio-lipids (Ojewumi et al., 2017). Among the established methods for biodiesel production, the most frequent process is transesterification. used industrial process due to its simplicity and its ability to lower viscosity (Ehiaguina et al., 2020). Transesterification involves reacting triglycerides in oil or fat with alcohol in the presence of a catalyst to form alkyl esters (Gandhi & Gogate, 2021).

However, challenges in commercializing biodiesel include the high cost of raw materials, which accounts for 70-88% of total production cost[(Nasya et al., 2021)**,** (Ehiaguina et al., 2020)**]**, and the reliance on edible oils, which could lead to a food shortage and global food market disparities (Helen et al., 2021). To address this, the use of non-edible oils like neem seed oil has been recommended to reduce production costs and prevent food-versus-fuel conflicts (Ehiaguina et al., 2020). Yet, the high acid content in many non-edible oils poses a challenge for direct transesterification. Low acidity oils (2.0 mg KOH/g of oil) are regarded as acceptable for biodiesel production, as higher acid values lead to soap formation instead of ester production, resulting in lower yields and more complex separation processes (Helen et al., 2021). Thus, esterification is necessary before using such oils used in the transesterification process to make biodiesel.

Esterification involves reacting FFAs in oil with low molecular weight alcohol and an acid catalyst to form esters, reducing the FFA content and improving the potential for transesterification (Mueanmas et al., 2018). Due to its crucial role, optimizing the esterification process has garnered significant attention (Prasertpong et al., 2020). Factors affecting esterification temperature, include time, catalyst concentration, and alcohol-to-oil ratio. Sulfuric acid is commonly used as a homogeneous acid catalyst(Ehiaguina et al., 2020).

Optimizing process parameters is a critical step to enhance efficiency (Gandhi & Gogate, 2021). After process modeling, optimization becomes key. Response Surface Methodology (RSM), a statistical tool, is commonly used to optimize and model chemical processes (Prasertpong et al., 2020). RSM reduces the number of experimental runs while investigating the impact of independent variables (factors) on the dependent variable (response). For this study, the dependent variable is acid value reduction, while independent variables include reaction temperature, catalyst loading, methanol/oil ratio, and time. RSM is also employed to examine interactions between variables and to achieve maximum production through mathematical modeling (Betiku et al., 2016).

- In this study, the goal was to reduce the high FFA content of non-edible Neem seed oil to ≤1% for biodiesel production using sulfuric acid as a homogeneous catalyst in an esterification process with methanol. RSM was used to analyze the influence of key parameters (temperature, catalyst dosage, methanol-to-oil ratio, and time,) on %FFA and optimize the process parameters.RSM was used to examine both the influence of the essential parameters (methanol-to-oil ratio, catalyst dosage, and time) on the %FFA of the oil and the optimization of the process parameters.

2. Materials and methods

2.1 Materials

The Neem oil used in this research work was obtained from National Research Institute for Chemical Technology, Zaria. (NARICT). However, chemicals/reagents of analytical grade with purity of about 99% from chemical engineering Ahmadu Bello University, Zaria were used. The chemicals/reagents used were: Methanol; H_2SO_4; NaOH; Isopropyl alcohol; Phenolphthalein and KOH.

2.2Design of experiment

In order to optimize the reduction of FFA in the neem oil, central composite rotary design (CCRD) of RSM was adopted using a two level-three factors (2^3), requiring 20 experiments which included six axial points, six central points, and eight factorial points, to provide information regarding the interior of the experimental region, allowing evaluation of the curvature (Gwi et al, 2009). The parameters selected for the reduction of FFA and their respective levels were as follows; Reaction time (60-120 minutes), Catalyst concentration (1.0-3.0 w/w,%) and methanol to oil ratio (0.20-0.60w/w,%) but temperature was kept constant at 60°C as shown in Table 2.1

Table 2.1- Parameters selected and their lower and upper limits

Factors	**Unit**	**Low level (-1)**	**High Level**
Catalyst Concentration	wt, %	1.00	3.00
Methanol/ oil ratio	w/w, %	0.20	0.60
Reaction time	Min	60.00	120.00

Table 2.2: Matrix design for the esterification reaction using actual values

Std	Run	Block	Factor 1 A:Reaction time min	Factor 2 B:catalyst conc. (w/w)%	Factor 3 C:methanol/oil ratio (w/w)%	FFA
12	1	Block 1	90.00	3.68	0.40	
5	2	Block 1	60.00	1.00	0.60	
4	3	Block 1	120.00	3.00	0.20	
1	4	Block 1	60.00	1.00	0.20	
20	5	Block 1	90.00	2.00	0.40	
11	6	Block 1	90.00	0.32	0.40	
10	7	Block 1	140.45	2.00	0.40	
19	8	Block 1	90.00	2.00	0.40	
15	9	Block 1	90.00	2.00	0.40	
3	10	Block 1	60.00	3.00	0.20	
18	11	Block 1	90.00	2.00	0.40	
6	12	Block 1	120.00	1.00	0.60	
14	13	Block 1	90.00	2.00	0.74	
13	14	Block 1	90.00	2.00	0.06	
17	15	Block 1	90.00	2.00	0.40	
8	16	Block 1	120.00	3.00	0.60	
9	17	Block 1	39.55	2.00	0.40	
2	18	Block 1	120.00	1.00	0.20	
16	19	Block 1	90.00	2.00	0.40	
7	20	Block 1	60.00	3.00	0.60	

* Values are to be determine experimentally

2.3Pre-treatment of neem oil

The neem oil obtained is a mixture consisting ofsolid particles, glycerides, free fatty acids, water,and many other impurities. The presence of such impurities creates challenges during both transesterification and esterifcation reactions resulting in lower yield of the sssbiodiesel. The procedure employed for the removal of these impurities are as follows:A heating mantle with a temperature setting of 100oC was used to heat up about 2 kg of the oil in a glass beakerand agitated for an hour at a speed of 450rpm. Water was removed from the oil by increasing the temperature to $130^{o}C$ for 10 minutes followed by cooling for 15 minutes. The cooled heated oil was filtered using a mesh of 100mm size to Eliminate solids and contaminants.

2.4 Choice of reaction conditions

In this work, all the experiments were carried out at atmospheric pressure, to avoid the production costs associated with high pressures. For most organic reaction such as esterification reaction, the rate of reaction increases with increasing temperature (Freedman *et al.*, 1984). The maximum operating temperature, however, must not be higher than the methanol's boiling point (64.7oC). For this reason, the maximum temperature chosen for the reactions was 60°C. The reaction time for all the experiments was 60-120 minutes and concentrations of the catalyst ranges from 1 to 3.0 wt%, according to the literature (Freedman *et al.*, 1984)

2.5 Esterification of the Neem oil

50g of neem oil was measured and poured in a conical flask using a weighing balance. The conical flask containing the neem oil sample was placed on top of a heating mantle with a magnetic stirrer, which agitated at a speed of 450 rpm and heated to a temperature of $60^{o}C$. A certain quantity of catalyst(H_2SO_4)was heated to 60oC after being dissolved in the necessary amount of methanol (Table 2.2 for the acid and methanol quantity). The heated mixture of (methanol + H_2SO_4) was added to the heated neem oil and timed immediately.

At the end of the reaction, the mixture was poured in a separating funnel and was allowed to settle for some time. Methanol, water and H_2SO_4 raised to the top of the separating funnel leaving the denser oil below. The oil was drained in a clean conical flask. The product sample of 5ml was taken, and the FFA was calculated and noted.The purpose of the pretreatment (esterification) is to lower the %FFA to be less than or equal to 1%.

2.5.1 Free fatty acid determination

1g of neem oil sample was weighed in a conical flask.25ml of propan-2-ol was added to the sample to dissolve the oil. The mixture was then given two drops of phenolphtalein indicator.

Prepared 0.1M of KOH was poured in the burette and titrated against the mixture of the neem oil sample. After a colour change was observed from yellow to pink, the initial and final readings were recorded, then the average titre value was calculated. The acid value was calculated using equation 2.1

$$Acid\ value\ = \frac{(molarity\ of\ KOH \times molar\ mass\ of\ KOH \times\ titre\ value)}{mass\ of\ oil} \text{..........................(2.1)}$$

From the above equation, the percentage free fatty acid value was obtained as:

$$\%\ FFA\ = \frac{acid\ value}{2} \text{..(2.2)}$$

3. Results and discussion

3.1 Development of model equation for the esterification reaction

Initially, the FFA value of the oil was found to be 4.77%, this FFA content of the raw oil was not within the specified ASTMD standard for biodiesel production. Therefore, there was the need to neutralize the FFA through esterification reaction with methanol in the presence of H_2SO_4 as a catalyst. The findings of the experiments carried out in accordance with the experimental plan shown in Table 2.2 is presented in Table 3.1. These results were entered into the Design Expert software for further analysis.

It is evident from Table 3.1 that different values of FFA were obtained at different reaction conditions. The lowest value of FFA (0.67) was obtained when the catalyst concentration was 2% (w/w), methanol to oil ratio of 0.4 and reaction time of 90 minutes. This value of FFA is within the limit specified by ASTMD and is desirable for transesterification reaction (Singh, 2009).

Table 3.1: The esterification reaction experimental findings utilizing actual values

Std	Run	Block	Time (A)	Catalyst (B)	MeOH/Oil (C)	FFA
			Min.	(w/w) %	(w/w) %	%
1	19	Block 1	60.00	1.00	0.20	2.11
2	8	Block 1	120.00	1.00	0.20	1.7
3	10	Block 1	60.00	3.00	0.20	1.94
4	4	Block 1	120.00	3.00	0.20	1.41
5	6	Block 1	60.00	1.00	0.60	0.76
6	9	Block 1	120.00	1.00	0.60	0.87

7	17	Block 1	60.00	3.00	0.60	0.73
8	12	Block 1	120.00	3.00	0.60	0.71
9	2	Block 1	39.55	2.00	0.40	2.1
10	20	Block 1	140.45	2.00	0.40	2.22
11	15	Block 1	90.00	0.32	0.40	0.72
12	14	Block 1	90.00	3.68	0.40	1.05
13	13	Block 1	90.00	2.00	0.06	1.73
14	3	Block 1	90.00	2.00	0.74	0.61
15	1	Block 1	90.00	2.00	0.40	0.76
16	11	Block 1	90.00	2.00	0.40	0.78
17	18	Block 1	90.00	2.00	0.40	0.74
18	7	Block 1	90.00	2.00	0.40	0.69
19	5	Block 1	90.00	2.00	0.40	0.76
20	16	Block 1	90.00	2.00	0.40	0.67

3.2 Statistical analysis of data

Analysis of variance (ANOVA) is commonly used to summarize the test performed for significance on the individual model coefficient, significance of the regression model, and lack-of –fit. Table 3.2 displays an ANOVA table for the FFA reduction response surface quadratic model. The response (FFA) ranges from 0.61 to 2.22%, (Table 3.1). The ratio of the maximum to minimum is 3.64. A ratio greater than 10 usually shows the need for transformation. Therefore, there is no need for transformation in this case.

Table 3.2: Response surface quadratic model ANOVA table

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	3.10	9	0.34	19.36	< .0001	significant
A	1.374E-003	1	1.374E-003	0.077	0.7868	
B	4.893E-003	1	4.893E-003	0.27	0.6116	
C	1.65	1	1.65	92.45	< .0001	
A^2	1.37	1	1.37	76.90	< .0001	
B^2	0.049	1	0.049	2.74	0.1289	
C^2	0.092	1	0.092	5.19	0.0459	
AB	0.010	1	0.010	0.57	0.4685	
AC	0.024	1	0.024	1.33	0.2751	
BC	2.834E-003	1	2.834E-003	0.16	0.6983	
Residual	0.18	10	0.018			
Lack of Fit	0.14	5	0.029	4.05	0.0753	not significant
Pure Error	0.035	5	7.046E-003			
Cor Total	3.28	19				
Std. Dev.	0.13	R-Squared	0.9457			
Mean	1.06	Adj R-Squared	0.8969			
PRESS	1.14	Adeq Precision	13.660			

The F value of 19.36 indicates that the model is significant (Table 3.2). Values of “Prob. > F” less than 0.05 indicates model terms are significant. In this case, the “Prob. > F” value is 0.0001 indicating the model equation is significant. Applying similar treatment to the model terms, MeOH/Oil ratio (C) and reaction time (A) were the only significant model terms associated with the reduction of FFA having “Prob. > F” value of 0.0001 which is less than 0.05. (Vicent *et al*, 1998). Other terms (catalyst concentration and its reciprocal interactions with other terms) were not significant and provide only secondary factor in the decrease in FFA. The correlation coefficient (R^2) value (0.9457) is relatively high, close to 1, which is desirable and is in reasonable agreement with the adjusted R^2 value (0.8969). The range of the expected values at the design points and the average prediction error are compared to determine adequate precision. Ratios above 4 signify sufficient model discrimination. In this instance, the value (13.660) is significantly higher than 4.

The final model equation in terms of coded values for the reduction of FFA in neem oil is shown in Equation (3.1).

$$\frac{1.0}{FFA} = 1.37 + 0.010 * A - 0.019 * B + 0.35 * C - 0.31 * A^2 - 0.058 * B^2 - 0.080 * C^2 + 0.036 * A * B - 0.054 * A * C + 0.019 * B * C \qquad (3.1)$$

3.3 Validation of the developed model

In order to regulate the accuracy of the model expanded, experimental data were substituted in the model equation at different conditions of catalyst concentration, MeOH/Oil ratio and reaction time and the corresponding predicted FFA reduction was obtained (See Table - 3.3).

Table 3.3- Comparison of actual and predicted values by the model

Standard Order	Actual Value	Predicted Value	Residual
1	0.47	0.58	-0.11
2	0.59	0.64	-0.051
3	0.52	0.43	0.081
4	0.71	0.63	0.075
5	1.32	1.35	-0.031
6	1.15	1.19	-0.037
7	1.37	1.28	0.094
8	1.41	1.26	0.15
9	0.48	0.48	-1.084E-003
10	0.45	0.51	-0.061
11	1.39	1.23	0.16
12	0.95	1.17	-0.22
13	0.58	0.56	0.022
14	1.64	1.72	-0.084
15	1.32	1.37	-0.050
16	1.28	1.37	-0.084
17	1.35	1.37	-0.015
18	1.45	1.37	0.083
19	1.32	1.37	-0.050
20	1.49	1.37	0.13

A parity plot in Figure 3.1 of experimental values vs predicted values showed high correlation coefficient of 0.9457 which is close to 1.0 indicating accuracy of the model developed within the experimental range studied.

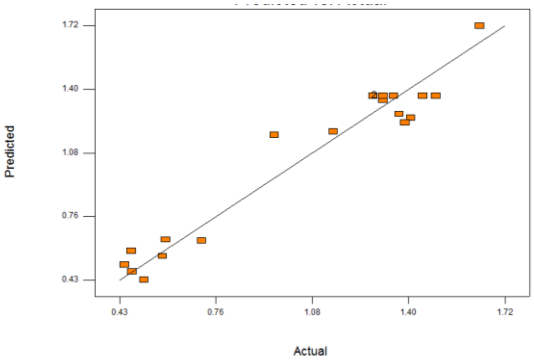

Figure 3.1: Parity plot of experimental and predicted FFA by the model developed

However, the developed model forecast that the best set of reaction conditions to obtained FFA of less than 1% at minimum methanol quantity (expensive reagent) were catalyst concentration of 1.0%,w/w), MeOH/Oil of 0.4 (w/w) and reaction time of 90 minutes.For the desired transestrification reaction, these experimental conditions lowered the FFA to as low as 0.67%.

3.4 Diagnostic plots

The normal probability plots of the residuals and the plots of the residuals versus the predicted response for free fatty acid reduction are presented in Figures 3.1 and 3.2.

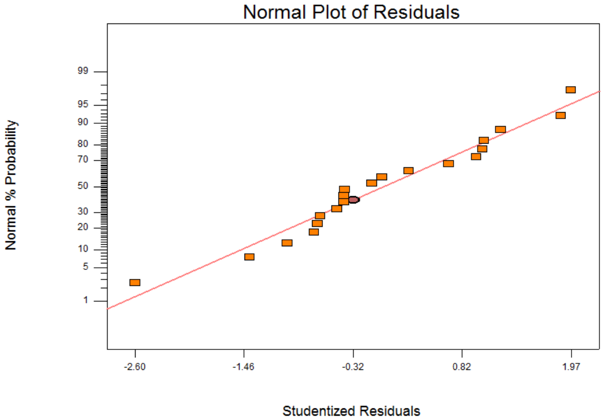

Figure 3.2:Normal probability plot of residuals

A check on the plots in Figure 2.2 shows that the residuals generally fall on a straight line signifies a uniform distribution of errors. Also Figure 3.3 revealed that the residuals have no clear pattern (unusual structure) and are evenly distributed in between the horizontal line marked (0.00). This suggested that the model proposed is adequate and there is no reason to suspect any violation of the independence or constant variance assumption (Noordin *et al.*, 2004)).

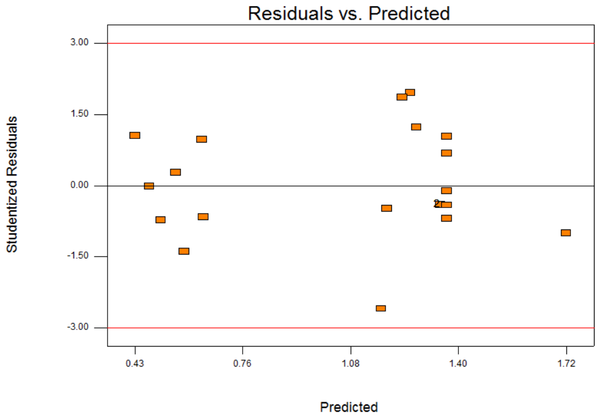

Figure 3.3: Plot of residuals versus predicted

3.5 Optimization of esterification reaction by response surface methodology

The response surface corresponding to the second-order model (Figure 3.4) shows that at any given catalyst concentration, the reduction in free fatty acid disclosed some linear dependency pattern at both high and low methanol-to-oil ratio (0.2 % w/w &0.6 % w/w). It is visible from Figure 3.4 that increasing methanol-to-oil ratio from (0.2-0.6 %) resulted in significant reduction in free fatty acid of the neen oil from1.1% to 0.63%. However, at the highest methanol-to-oil ratio of 0.6, the lowest free fatty acid obtained was 0.612 % at a catalyst concentration of 2.0 % (w/w).

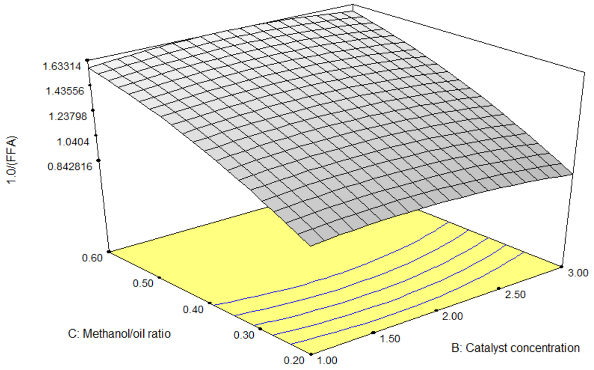

Fig 3.4: Effect of MeoH/Oil and catalyst concentration on FFA

This confirmed the fact that methanol-to-oil ratio had an important effect on FFA reduction of the neem oil. However, Catalyst concentration change above 1.0 weight percent had no effect on the free fatty acid reduction of the oil at any given methanol-oil-ratio. Water produced negatively impacts the esterification reaction, which could be improved by its continual removal from the mixture(Hanny *et al*., 2008).

It is also visible in Figure 2.5 that at low catalyst concentration (1.0 wt. %), there was moderate decrease in FFA of the oil as the reaction time increases from 60 minutes until it arrived somewhere with a 90-minute intermediate reaction time. This indicates that reduction in FFA is achieved with increase in reaction time up to 60 minutes. Beyond 90 minutes, the FFA sharply began to increase from about 0.75% to about 1.07% until when the reaction time reached 120 minutes

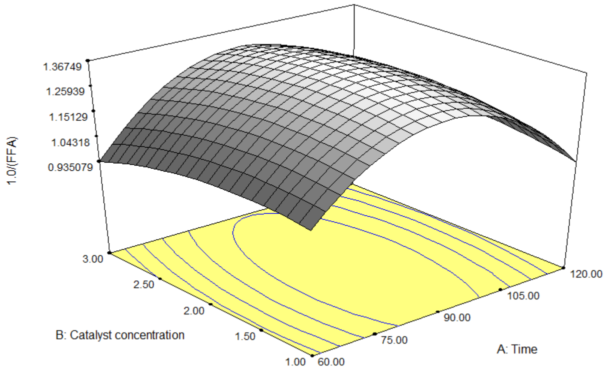

Figure 3.5: Catalyst concentration and reaction rate effects on FFA

This increased in FFA concentration of the neem oil beyond 90 minutes could be attributed to the addition of excess acid after the reaction must have been completed (Hanny *et al*., 2008). Similar behavior and pattern were also noticed as the catalyst concentration was raised above 1.0 weight percent. However, the lowest FFA of about 0.74 % was obtained at catalyst concentration of 1.0 wt.% and reaction time of 90 minutes. This indicates that the effect of catalyst concentration beyond 1.0 wt.% was not significant on the study of the decrease of FFA under the experimentally determined methanol-to-oil ratio and reaction time.

But at low reaction time of 60 minutes in Figure 3.6, there was gradual decreased in FFA of the oil as the methanol-to-oil was increased. Similarly, at high reaction time (120minutes), the FFA also decreased with increased in methanol-to-oil but was more significant at high methanol-to-oil than at low.

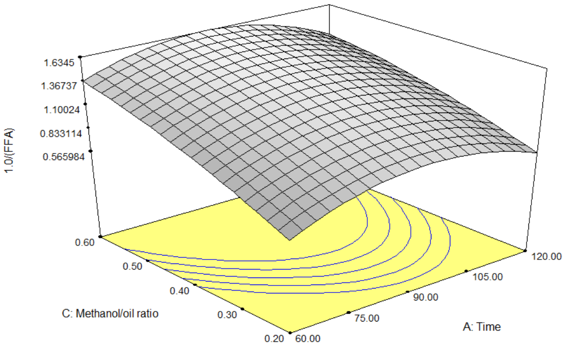

Figure 3.6: Effect of MeOH/Oil and reaction time on FFA

However, at any designated methanol-to-oil ratio, the FFA decreased as the reaction time increased until it reached somewhere at 90 minutes. Beyond 90 minutes, the FFA gradually increased until it reached 120 minutes. This shows that increased in reaction time after 90 minutes did not decrease the FFA of the oil. This also confirmed the fact that methanol-to-oil ratio and time are the most important factors affecting FFA reduction in Jatropha seed oil. Therefore, it can be concluded that the best operating conditions for this type of reaction is intermediate reaction time, higher methanol-to-oil ratio and lower catalyst concentration. However, numerical optimization of the reaction at optimum methanol-to-oil ratio predicted that to obtain free fatty acid of 0.78% which is suitable for transesterification reaction the following conditions holds; methanol-to-oil ratio=0.4 (w/w), catalyst concentration of 1.0 wt. % and reaction time of 90 minutes.

4. CONCLUSIONS

The present study explored the possibility of reducing the high FFA content of neem seed oil in an esterification process with sulfuric acid catalyst. RSM modeled and improved the procedure. The best-operating conditions with the min %FFA (0.67) established for the esterification process are a methanol-to-oil ratio of 0.4, catalyst concentration of 2 wt%, reaction time of 90 min, and temperature of 60 °C. The model developed is significant with F value of19.36 and R2 of 0.9896 and modified R2 of 0.8969 were determined to be adequately suitable to forecast the procedure. The min %FFA of the esterified neem oil showed that it can be used for biodiesel synthesis without soap formation. The findings of this current study could help in reactor design for industrial applications for the esterification process.

APPENDIX A

A.1 PREPARING KOH SOLUTION

0.1M of KOH solution was prepared using the relationship below:

Molarity = $\frac{mass}{molar\ mass}$…………………………………………………… A1

Molarity of KOH required = 0.1M
Molar mass of KOH = 56.1g/mol
Mass of KOH = Molarity of KOH required * Molar mass of KOH
Mass of KOH = 0.1mol/ml* 56.1g/mol
Mass of KOH =5.61g/ml
5.61gof KOH dissolved in 1000ml water
5.61 *250 will dissolve in 250ml of water = 1.4025g of KOH
1000
1.4025g of KOH was weight and dissolved in 250ml of water to obtain 0.1M of KOH.

APPENDIX B

Table B1: FFA calculation using Microsoft Excel

S/N	Avg. titer (cm^3)	K=1.4025(g)	Acid value (%)	FFA (%)
1.	1.50	1.4025	4.22	2.11
2.	1.21	1.4025	3.4	1.7
3.	1.38	1.4025	3.88	1.94
4.	1.01	1.4025	2.82	1.41
5.	0.54	1.4025	1.52	0.76
6.	0.62	1.4025	1.74	0.87
7.	0.52	1.4025	1.46	0.73

8.	0.51	1.4025	1.42	0.71
9.	1.50	1.4025	4.2	2.1
10.	1.58	1.4025	4.44	2.22
11.	0.51	1.4025	1.44	0.72
12.	0.75	1.4025	2.1	1.05
13.	1.23	1.4025	3.46	1.73
14.	0.43	1.4025	1.22	0.61
15.	0.54	1.4025	1.52	0.76
16.	0.56	1.4025	1.56	0.78
17.	0.53	1.4025	1.48	0.74
18.	0.49	1.4025	1.38	0.69
19.	0.54	1.4025	1.52	0.76
20.	0.48	1.4025	1.34	0.67

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