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PROCESS OPTIMIZATION OF BIODIESEL PRODUCTION USING CENTRAL COMPOSITE ROTATABLE DESIGN (CCRD) MODEL BY RESPONSE SURFACE METHODOLOGY (RSM)

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ABSTRACT

The study deals with the optimization, characterization and kinetic studies of biodiesel production from virgin moringa oleifera seed oil obtained from Northern Nigeria. The optimization of reaction variables was achieved through Central Composite Rotatable Design (CCRD) via Response Surface Methodology (RSM). The virgin oil was degummed prior to subjecting it for biodiesel production using methanol and sodium hydroxide. Reaction variables (reaction temperature, mole ratio, catalyst concentration and reaction time) were optimized using statistical software (Design Expert 7.0). Thirty (30) experimental runs were carried out using CCD. Optimal biodiesel yield (96.67%) was achieved at a reaction temperature, mole ratio, catalyst concentration and reaction time of 50 °C, 6:1, 0.25wt% and 60 minutes respectively. The statistical equation generated is in the form of second order

polynomial with R^2 value of 0.9215 which depicting 92.15% reliability of the second order polynomial equation obtained. These depicts that the experimental yields are in good agreement with predicted yields. Biodiesel fuel properties obtained showed that the density, specific gravity, viscosity, acid value, moisture content, sulphated ash, cetane number, cloud point, flash point, refractive index, distillation temperature (95 % recovery), initial boiling point and final boiling point are 0.860 gcm-3, 0.840, 4.90mm2s-1, 0.480mgKOHg-1, 0.096%, 0.020%, 44.00, -9^{o}C, 163^{o}C, 1.22, 330^{o}C, 130^{o}C, and 340^{o}C respectively. The reaction was found to obey first order kinetics with an average rate of reaction, and activation energy of 476.00 JK-1. The biodiesel properties and the kinetic parameters obtained compare favorably with standards spectra of biodiesel from literature and ASTM standards.

Keywords – Application; *Moringa Oleifera;* Optimization; Analysis of variance; Kinetics

1. Introduction

Africa, being one of the fastest growing continents in the world and with the huge energy demand is faced with the dire situation of exploring and exploiting all renewable and non-renewable energy sources to meet the needs of its ever-growing population. As of 2004, Africa was home to about 885 million people all spread around its 54 countries [1]. The critical nature of our energy demand, the depleting nature of fossil fuel reserves, as well as the problems associated with crude and its products have made the quest for alternative energy sources more imperative.

According to Annam [2], it is only through the exploitation of alternative energy sources that the problems associated with the use of fossil fuel can be tackled. Aransiola [3] also succinctly summarized the drive for alternative energy sources as the awakened consciousness for production of cleaner energy and the reduction of generation of associated pollutants which ultimately will lead to a better living environment and a healthier people. One of the most significant advantages or potentials associated with the introduction or adoption of renewable energy strategy is also the provision of cost-effective options for a low carbon, sustainable energy future for the world [4].

Energy is globally and fundamentally regarded as an index of economic, social and environmental sustainability. The availability of energy sources (conventional, biogas,

bioethanol and biodiesel) for domestic, industrial and transport consumptions is said to be a live wire for the continuous existence of man and the environment [5]. Conventional energy sources are characterized by threats that cut across instabilities in terms of supply and/or deflation. Additionally, increased global environmental protection, conservation and awareness on the effects of fossil fuels (petroleum and diesel) emissions and the associated health hazards (the release of carcinogenic compounds), has necessitated governments around the globe to actively and practically impose sanctions and restrictions on the levels of fossil fuels emissions and the need for alternative sources of energy [6]. The utilization of biofuels as alternative sources of energy is favoured by lesser emission rates compared to conventional fuels [7]. Consequently, the quests for biodiesel alternative from various feed stocks have led to the production of available and efficient fuels (biodiesel, biogas and bioethanol) that compete favourably with fossils.

Biodiesel production, as outlined by [8-10] provides that cleaner alternative to the use of fossil fuel given its non-toxic, renewable and biodegradable nature does not contain sulphur and provides better lubrication for most equipment. Another huge potential in the use of renewable energy as exemplified by biodiesel production is the advantages of rural revitalization, job creation as well as reduction in global warming amongst others [11]. Despite the overwhelming potentials and advantages associated with adoption of renewable energy sources as possible replacement to petroleum, especially as it pertains to biodiesel production from vegetable oil, there are areas of concerns. The ever-present demand for food security and sustainability is always a competing demand that needs to be appropriately weighed before industrial or large-scale utilization of food crops for energy production is contemplated and been justified.

2. Materials and Methods

2.1 Materials

Moringa Oleifera seed oil used in the study was purchased from Dorayi, a local market in Kano State, Nigeria. Chemicals and reagents used in this study were of analytical grade purchased from Steve Moore Chemicals, Zaria, Kaduna State, Nigeria which includes sulfuric acid (H_2SO_4) solution (95 % concentration, 1.83 g/ml), ammonium sulphate (132.14 molecular weight), and ethanol (98% pure). NaOH was used as a base catalyst.

2.2 Methods

58 ml of methanol in 100 ml of the oil was measured and introduced into the conical flask and heated to 60^{o}C. Then 0.75% of sulphuric acid was measured and added to the oil and stirred using a magnetic stirrer for 1 hr. The stirrer was stopped when the reaction time was complete and the methanol-water layer formed at the top was subsequently removed. Similarly, 100ml of the oil was first filtered and transferred to a reaction flask. A solution of 1 %w/v of sodium hydroxide-to-volume (100ml) and methanol to oil ratio of 1:5 was mixed and allowed to dissolve properly prior to mixing with the oil in the reaction flask. The mixture was stirred at 200 rpm using reaction temperature of 65^{o}C. After the reaction time was reached, the individual mixtures for each run were poured into a separation funnel and allowed to settle under gravity for 12 hrs overnight. Thereafter, the bottom layers in each of the samples (glycerine) were drained off and the top layers (biodiesel samples) were collected in a clean beaker. Again, a separation funnel was washed and dried and the methyl ester samples (biodiesel) were returned into the separating funnel for washing with warm water. Washings were continuously carried out until the wash water attains a pH of 7. Moreover, the biodiesel samples were collected in beakers and dried on hot plates at about 100^{o}C until all the water molecules present were evaporated and samples were allowed to cool [12].

2.2.1 Experimental Design

Response surface methodology (RSM) is a useful statistical technique which has been applied in research into complex variable processes [13]. It employs multiple regression and correlation analysis as tools to assess the effects of two or more independent factors on the dependent variables. Optimization of transesterifcation reaction was undertaken, where the reaction temperature, methanol-water molar ratio, catalyst concentration and reaction time were investigated within one hour and 200 rpm mixing intensity. In order to optimize the central composite experimental design (CCD), a 2^4 central composite design was employed in this study, which generates 30 experimental runs. Considering the treatments as in dependent variables, difference in means of each treatment that was compared at a significance level of p value 0.05 was considered throughout the study.

2.2.2 Optimization Process

The optimization of biodiesel produced from *moringa oleifera* seed oil to determine the effect of operating parameters on biodiesel yield. Namely: mole ratio, catalyst concentration, reaction time and temperature were investigated using experimental design. The optimization

was carried out via central composite rotatable design matrix (CCRD) and response surface methodology (RMS). The results were analyzed by means of design software (Design Expert) (7.0.0). Table 1 depicts the CCRD design matrix generated from Equation 1.

$$\alpha = \pm (2^k)^{1/4} \quad (1)$$

Where:

K = number of variables under study.

Table 2.1: Upper, Lower and Centre Levels of 2^4 Central Composite Design Variables

S/N	Variable(s)	Symbol(s)	-1	0	+1	-α	+α
1	Temp.	X_1	40	50	60	30	70
2	Mole Ratio	X_2	5:1	6:1	7:1	4.0	8.0
3	Cat. Conc.	X_3	0.5	0.75	1.0	0.25	1.25
4	Time	X_4	45	52.5	60	37.5	67.5

2.3 Kinetic Analysis of Biodiesel Produced

First and second order kinetics were tested using Equations 1 and 2 while Equation 3 was used for the determination of activation energy of the process. Consider the reaction;

$$A \longrightarrow \text{Products} \quad (1)$$

Suppose we wish to test the first – order rate of the following type:

$$-r_a = -\frac{dCA}{dt} = kC_A$$

For this reaction, separating variables and integrating we obtain;

$$-\int_{CAO}^{dCA} 1\frac{dCA}{CA} = k\int_0^t dt$$

$$\text{In}\ \frac{CA}{CAO} = kt$$

In terms of conversion, the rate equation becomes;

$$\frac{dX_A}{dt} = k(1 - X_A)$$

On re-arranging and integrating, we obtain:

$$-\ln(1 - X_A) = k\int_0^1 dt \qquad \text{Or} \qquad -\ln(1 - X_A) = kt \quad (2)$$

Plotting $-\ln(1-X_A)\ against\ time$, setting the intercept at zero, R^2 – value is obtained, the closer the R^2 - value to unity; the better the order of the reaction. Similarly,

$$2A \longrightarrow \text{Products} \qquad (3)$$

The defining second – order differential equation becomes;

$$-r_A = \frac{dC_A}{dt} = kC_A^2 = kC_{A0}^2(1 - X_A)^2$$

On integration, we have:

$$\frac{1}{C_A} - \frac{1}{C_{A0}} - \frac{1}{C_{A0}}\frac{X_A}{1-X_A} = kt \qquad (4)$$

Plotting $\frac{X_A}{1-X_A}\ against\ time$, setting the intercept at zero, R^2 – value is obtained, the closer the R^2 - value to unity; the better the order of the reaction

$$k = Ae^{-E/RT} \qquad (5)$$

Where:

A = Reactant

r = Rate ($molh^{-1}$)

C_A = Concentration of reactants (gl^{-1})

k = Rate constant ($molh^{-1}$)

t = Time (h)

C_{AO} = Initial concentration of reactants (gl^{-1})

X_A = Fractional yield (%)

In = Natural Logarithm

K = Slope

A = Arrhenius constant

E = Activation energy

R = Universal gas constant ($JK^{-1}mol^{-1}$)

T = Temperature (K)

3. Results and Discussion

3.1 Physicochemical Properties of *Moringa Oleifera* Seed Oil

The physical properties and composition analysis of the products obtained from both homogenous and heterogeneous catalysts were determined as per the ASTM standard test procedures and tabulated in Table 3.1. The density of the biodiesel produced was 0.760gcm^{-3}. This value falls within the value put forward by ASTM standard (0.800) for diesel oil and the value put forward by Oyerinde and Bello [14]. The specific gravity of the waste vegetable oil biodiesel produced was 0.854. The value recorded (0.8400) falls within the range of 0.9_{max} recommended by the ASTM. This trend is attributed to the difference of the oil used. However, the specific gravity obtained is a clear indication that the transesterification reaction has satisfactorily reduced the specific gravity of the feedstock used from 0.910 to 0.8400. The viscosity of the biodiesel produced from *moringa oleifera* seed oil was found to be 5.90mm^{2}s^{-1}. The value falls within the range of 1.90 - 6.0mm^{2}s^{-1} recommended by ASTM standard. However, this value is higher by 1.00 mm^{2}s^{-1} and 0.58 mm^{2}s^{-1} compared to the kinematic viscosities reported by Radha and Manikandan [15]. The differences in kinematic viscosities can be due to the use of different pre-treatment methods used. The value of the kinematic viscosity recorded in this study depicts that the conversion process has significantly reduced the viscosity of the raw material from 0.61mm^{2}s^{-1} to 4.90mm^{2}s^{-1}. Acid values indicate the methyl ester's long-term corrosiveness and stability. The lesser the acid value of the methyl ester produced from *moringa oleifera* seed oil, the higher the stability (quality) and vice-versa. The acid value recorded from *moringa oleifera* seed oil methyl ester is 0.480mgKOHg^{-1}. This value is 0.02mgKOHg^{-1} lower than the standard put forward by ASTM (0.5mgKOHg^{-1}). In the same vein, the value recorded is also lower than the 4.960mgKOHg^{-1} reported by Ibeto [16]. The lower acid value of the methyl ester produced can be attributed to the nature of the feedstock used. The maximum standard percentage moisture content in methyl ester is 0.05% by volume according to ASTM. The percentage moisture content of the methyl ester produced from *moringa oleifera* seed oil is 0.096% by volume. This value is quite lower than the ASTM standard maximum limit of 0.50% by volume. Hence, the *moringa oleifera* seed oil methyl ester produced is said to be clean, dry and efficient. The content of sulphated ash in the methyl ester produced from *moringa oleifera* seed oil was 0.02 % by weight. The value recorded is lower than < 0.004%wt reported in literature [15, 17]. Hence, the methyl ester produced can be termed as sulphur free because the value recorded (0.012%wt) is negligible. The Cetane number (CN) of the biodiesel produced from *moringa oleifera* seed oil was 44.00.

This value is slightly lower than the ASTM minimum standard CN for biodiesel (47.00). Therefore, slight ignition delay is expected whenever the biodiesel is subjected to use in a diesel engine. The Cloud point (CP) of the biodiesel produced was – 9^0C. This conforms to ASTM (D975) standard of 14.50^0C for petroleum-based diesel fuel. Hence, the biodiesel can be operational even in polar region where the temperature (atmospheric) is not greater than – 9.00^0C. The flash point of the biodiesel produced is found to be 163^0C. This compares favourably with the value (166min) put forward by ASTM (D 6751) standard. The refractive index (RI) obtained was 1.220 at wave lengths of 550 to 600rpm which is lower than the refractive index reported in literature [16]. The difference can be attributed to differences in physical, chemical properties and the binding energy of the feedstock used. The Distillation temperature (DT) value obtained at 90% recovery was 320^0C, this compares favourably with standards and the values reported in literature [17, 24].

Table 3.1: Physicochemical Properties of *Moringa Oleifera* Seed Oil

S/No	Properties	Unit(s)		ASTM
1	Density	gcm^{-3}	0.860	0.90
2.	Specific Gravity	-	0.840	-
3.	Viscosity @ 40 ^{0}C	mm^2S^{-1}	4.900	6.0_{max}
4.	Acid value	$mgKOHg^{-1}$	0.480	0.500
5.	Moisture content	%	0.096	0.50
6.	Sulphated Ash	%	0.020	0.05_{max}
7.	Cetane Number	-	44.00	47_{min}
8.	Cloud point	^{0}C	- 9.00	-3 to 12
9.	Flash point	^{0}C	163.00	$>100_{min}$
10.	Refractive index	-	1.220	-

3.2 Optimization Process

A total number of thirty (30) experimental runs were carried out for obtaining the actual experimental results for the optimization of *moringa oleifera* seed oil using sodium hydroxide (NaOH). Table 2 depicts the percentage yields of experimental and predicted results of the optimization of biodiesel production of *moringa oleifera* seed oil via response surface

methodology (RSM) through central composite rotatable design (CCRD) matrix. Experimental percentage yields obtained for all the experimental runs depicted close ranges with the predicted results (Table 3.2). To this end, whenever the predicted percentages of yields are closer to the percentage experimental yields, it has become more than apparent that the statistical model development seeking to establish valid correlations between the operating parameters (mole ratio, catalyst concentration, time and temperature) is said to be reliable [18]. However, from Table 3.2, it is deduced that practical percentage yields biodiesel produced from *moringa oleifera* seed oil at the points of factorization are in line with the statistically predicted percentage yields except for an experimental run 9 (-1, -1, -1, +1), where the actual experimental yield recorded was 60.00% and the corresponding statistically predicted yield was 65.13%. According to Dhamesh and Math [19], lower temperatures are capable of hindering mass transfers needed to complete the reaction. Therefore, this phenomenon is attributed to the use of lowest conversion temperature (40°C), lowest mole ratio (5:1), lowest catalyst concentration (0.5%) while at the same time employing the highest reaction time (60min). It is also observed that biodiesel yields from *moringa oleifera* seed oil decrease with increase in catalyst concentrations. This trend is attributed to the fact that, the higher the amount of catalyst, the more the triglycerides react with the catalyst thereby forming soap and subsequently leads to decrease in yields [20]. Additionally, the higher the amount of catalyst, the higher the pH of the methyl ester produced. This often leads much washing of the methyl ester for removing deposited catalyst which often leads to loss of the biodiesel produced [18].

The ranges for percentage experimental yields recorded of the sixteen (16) points factorized were 47.00% to 96.00%. On the other hand, the ranges for percentage predicted yields were 46.38% to 90.71% through a combination point (+1, +1, +1, +1). This combination recorded maximum process variables. Temperature and time have positive effect on the percentage yield of biodiesel produced, contrary to the findings of Alhassan [21]. This variation is attributed to the use of different seed oils. Hence, optimum methyl ester yields at elevated temperatures are mainly the degradation of *moringa oleifera* seed oil viscosity thereby increasing the rate of the reaction while at the same time increase the yield [22].

Annam [2] conducted a study on the optimization of algal biodiesel reaction parameters using response surface methodology and reported 95.00% yield while Alhassan [21] reported a mean experimental yield of 91.76 ± 5.85% as the optimum yield of methyl ester from *Gossypium arboreum* seed oil biodiesel. In the same vein, Dhamesh and Math [19] carried out a study on the application of response surface methodology for optimization of biodiesel

production by transesterification of animal fat with methanol. The authors reported an optimized methyl ester yield of 85.93%. Wan-Omar [23] conducted a two-step RSM biodiesel production from waste cooking oil and reported an optimum yield of 81.30%. Also, Subhalaxmi [24] conducted a study on the optimization of reactive extraction of castor seed to produce biodiesel using response surface methodology (RSM) and reported 98.60% optimum yield. Moreover, Xiaohun [25] studied biodiesel production from crude cottonseed oil: an optimization process using response surface methodology (RSM) and reported 97% as the actual optimal yield of methyl ester from virgin cotton seed oil while Sharma [20] reported an optimum yield of 97.43% conversion of biodiesel from *Pongamia pinnata* oil using heterogeneous catalyst. The authors attributed the yield to the efficiency of heterogeneous catalyzed developed. This study obtained an overall optimum experimental biodiesel yield of 95.00% which was lower compared to the optimum predicted yield of 96.67%. Though the experimental yield in this study seems low compared to other virgin vegetable oils, the use of heterogeneous catalyst will ultimately improve the yield.

Table 3.2: CCRD Experimental Matrix depicting Observed and Predicted Yields

Run(s)	Factor 1 (X_1)	Factor 2 (X_2)	Factor 3 (X_3)	Factor 4 (X_4)	Actual Yield (%)	Predicted Yield (%)
1	-1	-1	-1	-1	75.00	75.54
2	+1	-1	-1	-1	82.00	85.46
3	-1	+1	-1	-1	83.00	84.96
4	+1	+1	-1	-1	86.00	86.88
5	-1	-1	+1	-1	57.00	59.79
6	+1	-1	+1	-1	78.00	79.71
7	-1	+1	+1	-1	77.00	76.71
8	+1	+1	+1	-1	90.00	88.63
9	-1	-1	-1	+1	60.00	65.13
10	+1	-1	-1	+1	84.00	84.54
11	-1	+1	-1	+1	82.00	80.54
12	+1	+1	-1	+1	91.00	91.96
13	-1	-1	+1	+1	47.00	46.38

14	+1	-1	+1	+1	74.00	75.79
15	-1	+1	+1	+1	69.00	69.29
16	+1	+1	+1	+1	91.00	90.71
17	-α	0	0	0	64.00	61.83
18	+α	0	0	0	95.00	93.17
19	0	-α	0	0	78.00	72.33
20	0	+α	0	0	95.00	96.67
21	0	0	-α	0	95.00	91.00
22	0	0	+α	0	74.00	74.00
23	0	0	0	-α	73.00	70.17
24	0	0	0	+α	63.00	61.83
25	0	0	0	0	81.00	73.00
26	0	0	0	0	74.00	73.00
27	0	0	0	0	65.00	73.00
28	0	0	0	0	73.00	73.00
29	0	0	0	0	67.00	73.00
30	0	0	0	0	78.00	73.00

3.2 Analysis of Variance (ANOVA)

Statistical analysis of variance on the optimization of biodiesel production from *moringa oleifera* seed oil using NaOH was employed mainly for estimating the effects of major reaction parameters relative to methyl ester yield. Table 3.3 depicts the response surface reduced cubic equation based on partial statistical sum of squares type III. According to Noordin [22] partial statistical sum of squares is said to be the sum of squares relative and corresponding to each and every effect adjusted for each and every other effect in the statistical equation selected after reproducibility test of the equation often suggested by the software used (Design Expert 7.0.0) and relatively compared with the results obtained; whereas the terms that appear insignificant in the equation are often corrected automatically via backward(s) cum stepwise(s) correction equation. From the results obtained, it is statistically clear that the four (4) reaction variables under study (mole ratio, catalyst

concentration, time and temperature) cum the statistical equation appear to be statistically significant p<.01. In statistics, a P-value lesser than 0.05 is a clear indication that the statistical equation generated is significant because of reasonably large number of every significant term needed to indicate effects on the responses and were sufficiently and reasonably enough to represent the actual relationship between the response and the independent variables [22]. The intercept recorded from the coefficient estimate showed 73.00%. The major effects of the variables (mole ratio, catalyst concentration, time and temperature) depict significances of p <.01. Hence, the relationship of the variables under study in the prediction of the linearity of independent factors and their interactions in surface response is represented by second order polynomial equation (Equation 2) [27].

$$Y = \alpha_O + \Sigma_{i=1}^{3}\alpha_1 x_1 + \Sigma_{i=1}^{3} x_{ii} x_2^2 + \Sigma\Sigma_{i<j=1}^{3}\alpha_{ij} x_i x_j \qquad (2)$$

Where:

Y = Biodiesel Yield

α_o = Intercept

xi and x_j = uncoded independent variables

α_i, α_{ii} and α_{ij} = linear, quadratic and interaction constant coefficients respectively

Table 3.3: Analysis of Variance

Source	Sum of Squares	df	Mean Square	F - Value	P – Value	Remark
Model	3769.05	14	269.22	12.57	< 0.0001	Significant
A-Temp.	*1472.67*	*1*	*1472.67*	*68.76*	*< 0.0001*	Significant
B-Mole Ratio	*888.17*	*1*	*888.17*	*41.47*	*< 0.0001*	Significant
C-Cat. Conc.	*433.50*	*1*	*433.50*	*20.24*	*0.0004*	Significant
D-Time	*104.17*	*1*	*104.17*	*4.86*	*0.0434*	Significant
AB	*64.00*	*1*	*64.00*	*2.99*	*0.1044*	Not Significant
AC	*100.00*	*1*	*100.00*	*4.67*	*0.0473*	Significant
AD	*90.25*	*1*	*90.25*	*4.21*	*0.0580*	Not Significant
BC	*56.25*	*1*	*56.25*	*2.63*	*0.1259*	Not Significant
BD	*36.00*	*1*	*36.00*	*1.68*	*0.2144*	Not Significant
CD	*9.00*	*1*	*9.00*	*0.42*	*0.5266*	Not Significant

A^2	*34.71*	*1*	*34.71*	*1.62*	*0.2223*	Not Significant
B^2	*226.71*	*1*	*226.71*	*10.59*	*0.0053*	Significant
C^2	*154.71*	*1*	*154.71*	*7.22*	*0.0169*	Not Significant
D^2	*84.00*	*1*	*84.00*	*3.92*	*0.0663*	Not Significant
Residual	*321.25*	*15*	*21.42*			
Lack of Fit	*131.25*	*10*	*13.12*	*0.35*	*0.9283*	Not Significant
Pure Error	*190.00*	*5*	*38.00*			
Cor Total	4090.30	29				
R – Squared	0.9215					

3.3 Effects of Operating Parameters on Biodiesel Yield

From the ANOVA analysis (Table 3.3), it is deduced that mole ratio, catalyst concentration, reaction time and temperature are significant independent variables. Also, the interaction of mole ratio and reaction time (AC) are significant for first (1st) order polynomial whereas mole ratio and catalyst concentration (AB); mole ratio and reaction temperature (AD); catalyst concentration and reaction time (BC); catalyst concentration and reaction temperature (BD) and reaction time and temperature (CD) are not significant for first order polynomials. It has become more than apparent that AC has effect on biodiesel yield (response). For a variable to be significant in 1st order polynomial and vice-versa, it does not statistically signify acceleration effect or deceleration effect on the yield of methyl ester, instead it only signifies that whenever such a variable is intensified and vice-versa, a corresponding increase or decrease is expected in the outcome, that is, biodiesel yield. It is conveniently deduced from the analysis statistical results that process variables: mole ratio (A) and time (C) and their interaction effects have much more impact on the yield biodiesel produced from *moringa oleifera* seed oil than catalyst concentration (B) and reaction temperature (D). Similarly, Figure 1 depicts the combination of the 3D response surface plots between the quantities of reaction parameters. It can be deduced that the yield of biodiesel recorded higher percentage value at higher operational values of time and temperature at constant catalyst concentration and mole ratio and vice-versa. The response surface plots of the optimization process were plotted for the effect of two (2) variables at a time while keeping others constant.

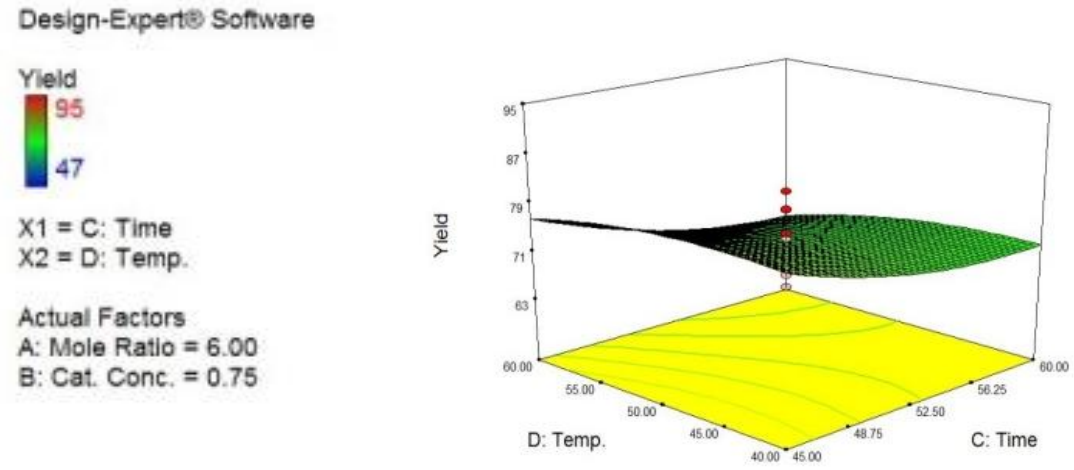

Figure 3.1: The effect of temperature and time on percentage yield.

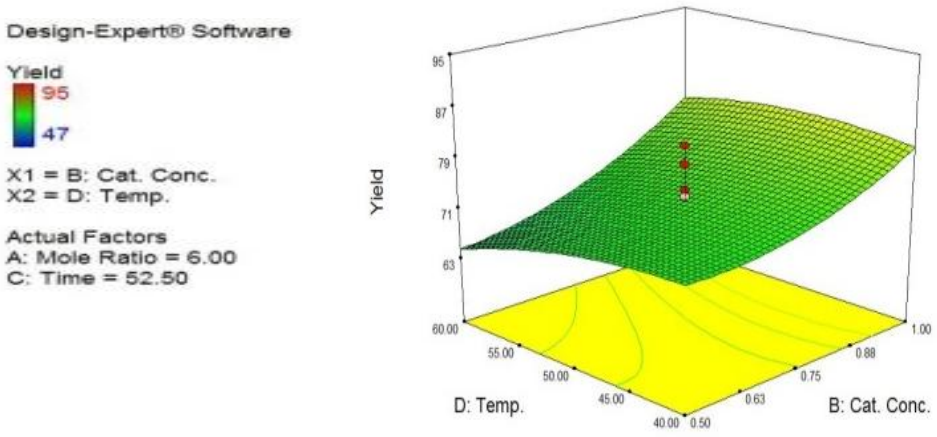

Figure 3.2: The effect of temperature and catalyst concentration on percentage yield.

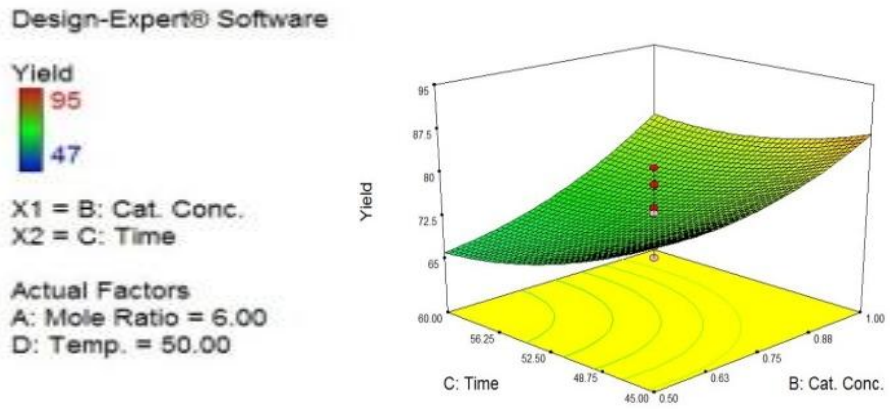

Figure 3.3: The effect of time and catalyst concentration on percentage yield.

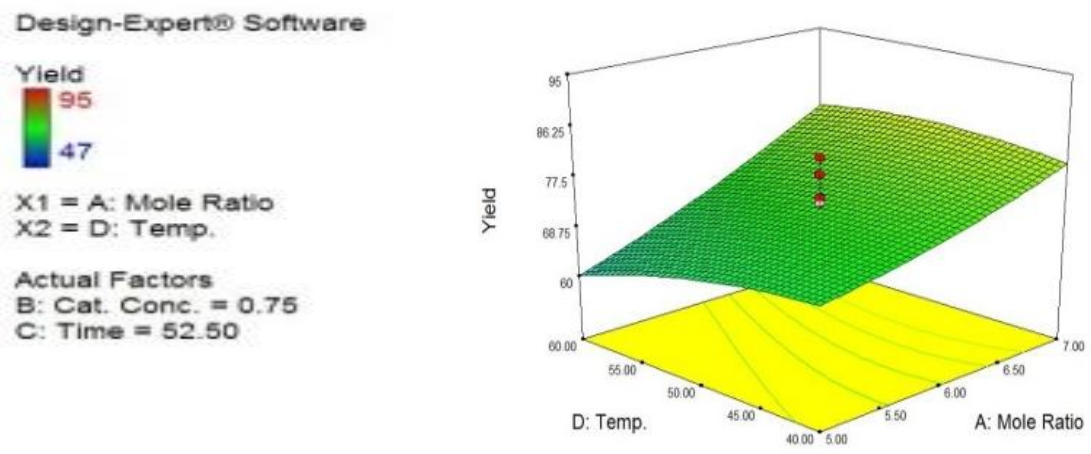

Figure 3.4: The effect of temperature and mole ratio on percentage yield.

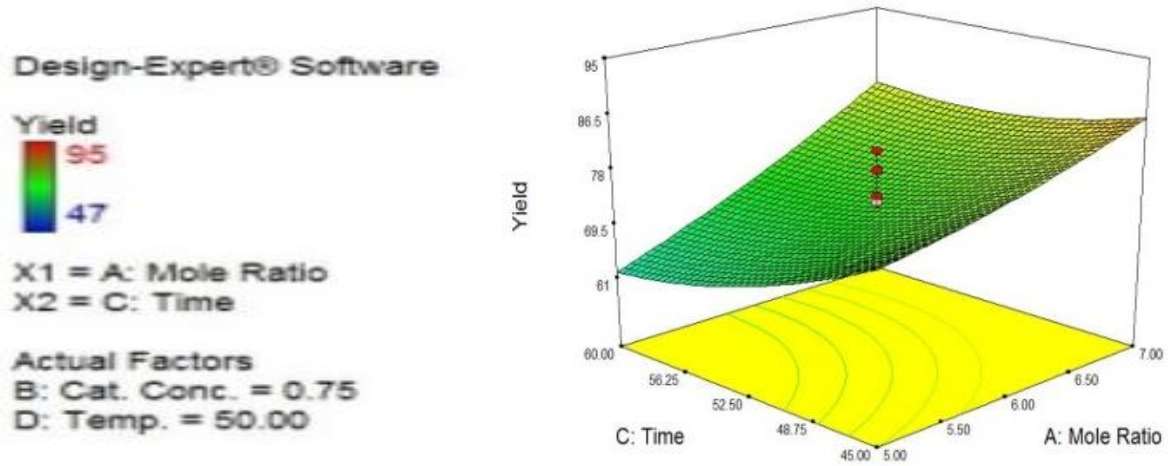

Figure 3.5: The effect of time and mole ratio on percentage yield.

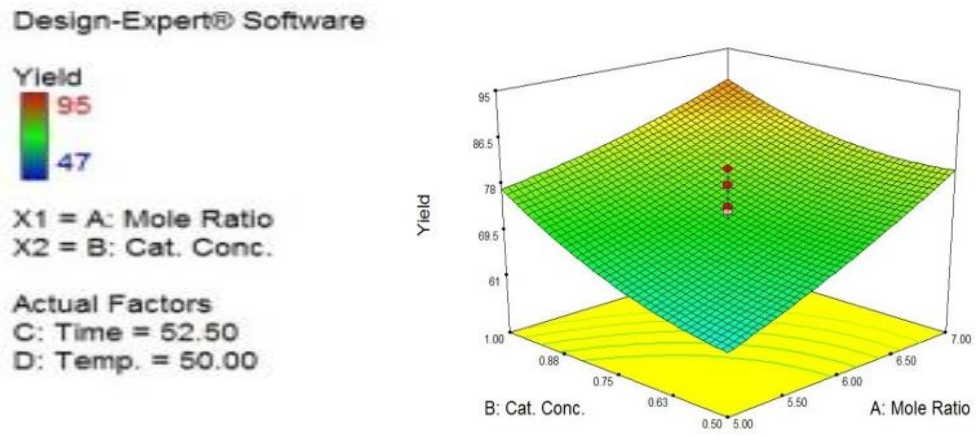

Figure 3.6: The effect of catalyst concentration and mole ratio on percentage yield.

3.4 Statistical Response Equations in terms of Coded and Actual Factors

For ascertaining the independent and interactive contributions of the variables under study (mole ratio, catalyst concentration, reaction time and temperature), the linear statistical response model is used for both values (coded and actual) of the methyl ester yield. Equations 3 and 4 depict the response equation in terms of coded and actual factors respectively. The linear statistical models depict the coefficients of all the variables in the linear regression equations, their statistical significances and their corresponding impacts on the yield of biodiesel from *moringa oleifera* seed oil. According to Roseli [28], the positive and/or negative signs attached to individual terms and their interactions are indications of synergistic and antagonistic effects on the methyl ester yield.

$$Yield = +73.00 + 7.83A + 6.08B - 4.25C - 2.08D - 2.00AB + 2.50AC + 2.38AD + 1.88BC + 1.50BD + .75CD + 1.13A^2 + 2.88B^2 + 2.38C^2 - 1.75D^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

$$Yield = +362.79167 - 29.04167 * \mathrm{M} - 79.16667 * \mathrm{C} - 7.25000 * \mathrm{T} + 0.19167 * \mathrm{t} - 8.00000 * \mathrm{M} * \mathrm{C} + 0.33333 * \mathrm{M} * \mathrm{T} + 0.23750 * \mathrm{M} * \mathrm{t} + 1.00000 * \mathrm{C} * \mathrm{T} + 0.60000 * \mathrm{C} * \mathrm{t} - 1.00000 * \mathrm{e}^{-002} * \mathrm{T} * \mathrm{t} + 1.12500 * M^2 + 46.00000 * C^2 + 0.042222 * T^2 - 0.017500 * t^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$$

Where

M= Mole Ratio

C= Catalyst Concentration

T= Time

t= Temperature

3.5 Reliability of the Statistical Model for the Optimization of Biodiesel Production from *Moringa Oleifera* Seed Oil using NaOH

To determine the reliability of the statistical model for the optimization of biodiesel production from *moringa oleifera* seed oil, the coefficient of determination otherwise known as R-squared (R^2) value is paramount because it indicates the fitness of the linear regression model developed. As a rule of thumb, the closer the R-squared value to unity, the higher the precision of the model. However, Table 3 depicts R^2 value of 0.9215. It is deduced that 92.15% of the methyl ester produced has been accounted for by the linear regression equation generated while 7.85% of the entire variations experienced on the response of the biodiesel produced could not be explained by the linear regression equation generated. Additionally, the

reliability of the linear regression model is ascertained by the values of standard deviation (4.63); the mean (76.70) and the adjusted R^2 value (0.8482). All the statistical information gathered were employed for predicting the optimum response of the biodiesel produced. Summarily, the outcomes have shown that the optimal response of biodiesel obtained for experimental result was 95.00±1.67% at a confidence level of 95.00%. Figure 3.7 depicts the probabilities of evaluating the optimum points of the actual and the predicted yields while Figure 3.8 depicts the parity plot of experimental (actual) yields versus the predicted yields for the total number of experiments carried out during the study. The contour plots are also significant mechanisms used in the interpretation of the interactions of two (2) variables at a time while keeping the others constant.

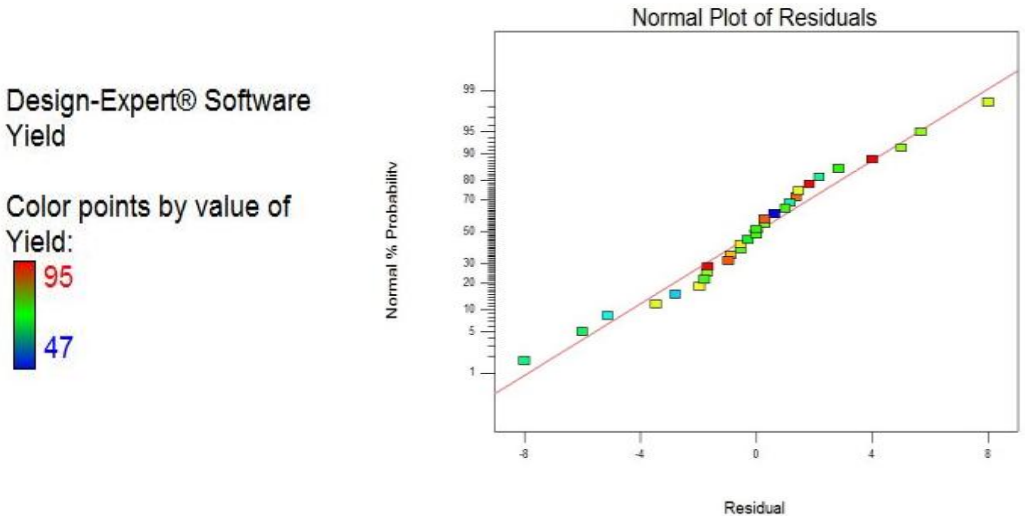

Figure 3.7: Normal and Probability Plots of Residuals

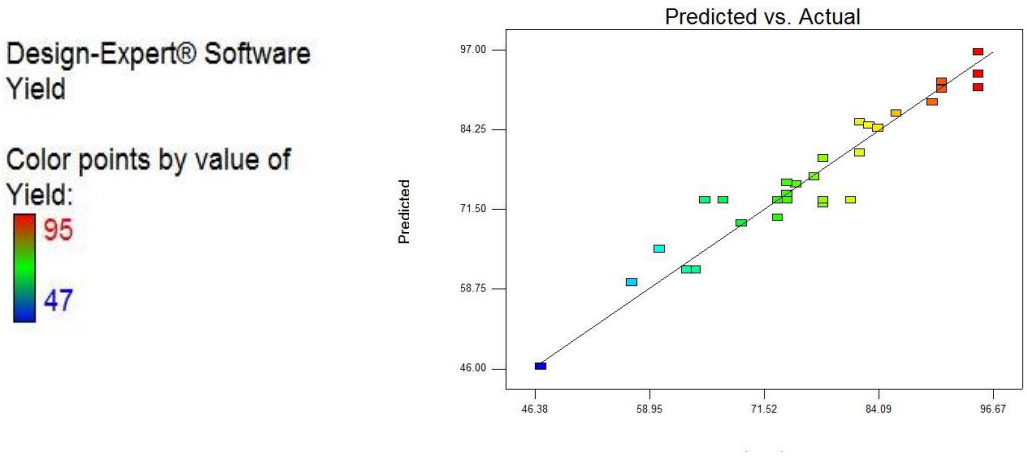

Figure 3.8: Plots of Predicted Biodiesel Yields versus Actual Biodiesel Yields

3.9 Kinetic Analysis of *Moringa Oleifera* Seed Oil Biodiesel

Kinetic analyses of *moringa oleifera* seed oil biodiesel production was carried out via empirical approach method. This method is visible because it describes the relationship of the operating parameters to the final quantity of the biodiesel produced.

3.9.1 Order of the Reaction

First and second order kinetics using empirical (integral) approaches were tested between 30°C to 60°C while equations 3.9, 3.10 and 3.12 were used for the determination of first order kinetics, second order kinetics and the determination of activation energy (E_a) of the production process respectively. The production of biodiesel from *moringa oleifera* seed oil obeys first order kinetics with an average rate of reaction 0.04 min^{-1}, the reaction proceeds faster at elevated temperatures. The calculated activation (E_a) recorded is 476.0 JK^{-1}. Figure 3.9 depict the R^2 value obtained for the determination of thermodynamic properties at 60°C while Table 3.4 depicts the summary of first and second order parameter obtained from the reaction.

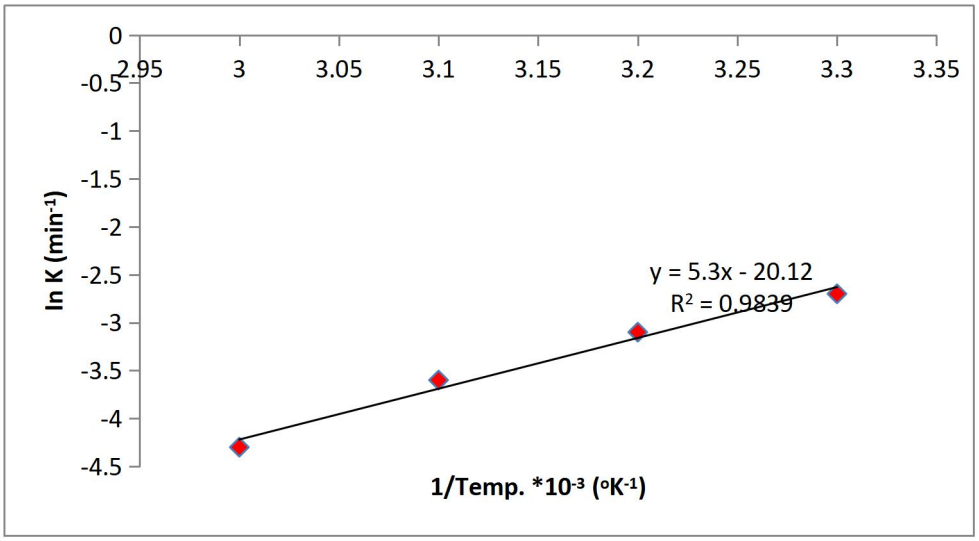

Figure 3.9: R^2 Value obtained for the Determination of Thermodynamic Properties at 60°C

Table 3.4: Summary of First and Second Order Kinetic Parameters

S/N	Temp. (°C)	R – Squared	
		First (1st) Order	Second (2nd) Order
1	30	0.5858	0.3224
2	40	0.6138	0.3568

3	50	0.5428	0.4098
4	60	0.5138	0.5724

4. Conclusion

Central Composite Rotatable Design (CCRD) via Response Surface Methodology (RSM) was applied for the optimization of reaction parameters (reaction temperature, mole ratio, catalyst concentration and reaction time) for the transesterification of *moringa oleifera* degummed virgin oil. The maximum yield obtained was 96.67% at reaction temperature, mole ratio, catalyst concentration and reaction time of 50°C, 6:1, 0.25wt% and in 60minutes respectively. Second order polynomial equations in terms of coded and actual factors were obtained for the prediction of biodiesel yield from *moringa oleifera* seed oil. By virtue of the R^2 values, mean and standard deviation, it has become more than apparent that the experimental yields obtained are in good agreement with the predicted yields therein. The biodiesel properties and the kinetic parameters obtained conform to both literature and standard biodiesel specifications and hence, biodiesel production from *moringa oleifera* seed oil is a viable alternative.

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