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Characterization and Optimization Study of Transesterification of Non-Edible Oil Using Response Surface Methodology

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ABSTRACT

In this study, calcium oxide (CaO) derived from waste bone was utilized as a catalyst for the transesterification of Neem seed oil (NSO) with methanol. The catalyst was characterized by scanning electron microscope (SEM), Fourier transforms infrared spectroscopy(FTIR), X-ray diffractometer(XRD) and Thermogravometric/differential thermal analysis. The process was optimized using response surface methodology (RSM) in combination with central composite design (CCD) was carried out to ascertain the best performing states and to improve the methyl ester output. The response changes being improved were: catalyst, concentration, methanol to oil molar ratio, reaction temperature, reaction time and agitation speed. The transesterification process was optimized by response surface methodology (RSM) in combination with the central composite design approach. From the analysis of variance (ANOVA), it was observed that the most significant criterion on methyl ester produced from methanolysis of neem oil was methanol to oil molar ratio and agitation speed. The predicted=91.2% output was established in good agreement with the analytical value of 92.0%, with R-squared value: 0.9966, Adj.R-squared value: 0.9904 and predicted R-squared value: 0.9846. The best methyl ester yield of 92.0% was achieved at 4h reaction time, with 4wt. % of catalyst weight and methanol to oil molar ratio of 8:1.

Key Words: *Biodiesel, Catalyst, Neemseed oil, Optimization, Response surface methodology, Transesterification.*

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1. INTRODUCTION

The globe's fossil oil substitute and intensifying ecological unease has generated a significant order for ecofriendly benign renewable energy resources [1]. There is an intensifying global demand for environmental policy and for the preserving of non-refillable raw materials. For this cause the probability of expanding possible energy origin to restore conventional petroleum has been received a wide attentiveness in the last few decades [14]. Methyl ester is deemed as a feasible substitute and subsequent combustible for internal combustion engine suitable to the anticipated scarcity of nonrenewable fuel source and rise in the cost of the petroleum.

It is ecofriendly, sustainable, non-toxic, ecologically-friendly, and has high flash point, better lubrication, high cetane number and has quite comparison in regard with substantial and synthetic attribute with that of standard diesel fuel [2]

Biodiesel is produced through a chemical process known as transesterification of different vegetable oil or animal fat with a short chain alcohol, in which one mole of glyceride reacts with three moles of alcohol in the presence of appropriate amount of catalyst to form mono methyl ester and glycerol [3,4,6].

The most common alcohols widely used are methyl alcohol and ethyl alcohol. Methanol, found frequent application in the commercial uses because of its low cost and its physical and chemical advantages [3]. Another advantage of using methanol is the separation of glycerine, which can be obtained through simple decantation [9].

There are several parameters that affect the yield of biodiesel through transesterification of vegetable oils. They are catalyst concentration, methanol to oil ratio molar ratio, reaction time and reaction temperature.

The experimental work carried out and reported in this paper was aimed at obtaining the most favorable production conditions for base catalyzed transesterification of methyl ester from neemseed oil. The investigations were carried out and established using response surface methodology (RSM) in combination with central composite design (CCD) and in addition, was utilized to study the correlation linking the variables and to ascertain the best state for most favorable production of biodiesel from neemseed oil with methanol in the presence of CaO (acid activated) derived from waste bone.

2. MATERIALS AND METHODS

2.1. Materials

The non-edible neem seed oil was purchased from National Research Institute for Chemical Technology (NARICT) Zaria, Kaduna state, Nigeria and the waste bones was sourced from a local market (Kubwa village market), Kubwa, Abuja. All chemicals-- H_3PO_4, NaOH methanol, were of analytical reagent grade and 99% pure. The equipment used include Petri dish, various sizes of beaker, different sizes of measuring cylinders, thermometer, pipette, hot plate with magnetic stirrer arrangement used as a heating and stirring device, separating funnel, digital weighing balance, stop watch, laboratory oven, filter paper ,cotton wool, masking tape, conical flasks, gas chromatography and mass spectroscopy(GC–MS), fourier transform infrared (FTIR) ,scanning electron microscopy(SEM),thermal gravimetric/differenetial thermal analyzer(TGA/DTA),x-ray diffractometer(XRD),x-ray fluorescence(XRF) etc.

2.2. Catalyst Preparation and Activation

The catalyst (waste animal bones) from goats was sourced from a local market in Kubwa, Abuja. The sourced waste bones were soaked in boiling water for several hours (6-8 hours) at about 75^0C to eliminate tissues and fats in the bone and then rinsed with distilled water for 3-4 times to remove dust and impurities. The waste bones were dried in the drying oven at 110^0C for 4hours to remove water and moisture before being ground finely to a <2mm particle size powder using a hammer mill. The crushed and powdered catalysts was sieved using various mesh sizes (100-200) to get particle of uniform size of mesh screens. The Sample of the crushed/powdered waste bone was calcined in a muffle furnace at variable temperature range of 400^oC, 500^oC, 600^oC 700^oC and 800^oC under static air with a heating rate of 10^OC/min for 4hours to state the effect of the calcination operations on modification of calcium species into hydroxyapatite (HAP) and to remove any absorbed water.

2.3. Catalyst Screening

The performance of the reactants was primarily examined under constant operating states. In order to select catalyst with better loading. Transesterification reaction was performed under constant operating variable conditions: Refined neem oil (30ml), methanol to oil molar ratio of 6:1, temperature of 55^0C, and 4 hr reaction time. Best performing catalyst that provide high fatty acid methyl ester yield was then selected for further experiment.

2.4. Catalysts Characterization

The Scanning electron microscope (SEM) investigation was carried out by Phenom Prox. The principal technique was applied to investigate the morphological composition and the nanoscopic quality of the catalysts. The peak aim use of SEM makes it to be essentially used for producing depiction of substances.

FTIR spectroscopy was used to relate the chemical structure and functional groups of neem oil, catalyst, and the produced biodiesel using KBr pellet method (Perkin Elmer Infrared Spectrometer). The samples were examined using spectrophotometer with ranges 650-4000cm-^{1} after 16 scans using a design of 8 cm-^{1} .KBr was used as background material in the analysis to take off signal noise. The blend was filled and compressed into a thin semi-transparent circular disk under 55 MPa of pressure in the disk. The disk was filled into the FTIR specimen plate and scanned. FTIR spectra were recorded using FTIR spectrophotometer.

The powder X-ray diffraction (XRD) investigation was carried out by using a Shimadzu diffractometer model XRD-6000 which was fitted with a diffracted-beam graphite monochromatic. The XRD sample was generated from crushed specimen following Cu-Kα radiation screening over a study span of 4 to 90^o. The thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris diamond thermo gravimetric/differential thermal analyzer (TG/DTA). A microgram aggregate of sample was placed on the weighing arm and closed up. The TGA procedure scaled the transformation of the sample weight as temperature changes. The heating temperature was from 30˚C to 950˚C at 10˚c/min.

2.5. Transesterification Process

The transesterification reaction was carried out in a three necked 250 ml round bottom flask fitted with a thermometer, condenser and a mechanical stirrer whose speed was also controlled The neemseed oil reacts with methanol in the presence of catalyst derived from waste of animal bone to produce biodiesel and glycerol. The refined neemseed oil (30ml) was measurably carried into a flat bottom flask placed on a hot magnetic stirrer. Then fixed quantity of catalyst (by weight of refined neemseed oil) was liquefy in the needed quantity and methanol was added. The reaction vessel was kept on a hot magnetic stirrer under fixed

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temperature with established stirring all-round the reaction. At designate time of 1-2 hours, the experiment was taken out, cooled, and the methyl ester in the upper layer was segregated from the result (i.e. the glycerol in the bottom layer) by settlement overnight under ambient condition. The percentage of the biodiesel yield was determined by comparing the weight of layer biodiesel with the weight of refined neemseed oil used.

The percentage conversion of each sample was calculated from the below equation[16].Yield (%) = $\frac{\text{Weight of methylester}}{\text{Weight of oil used}}$x100 (1)

2.6. Design of Experiment

The response surface methodology (RSM) in combination with central composite design (CCD) was utilized to improve the methyl ester production from neemseed oil. The 2-level -5- factor investigational pattern was utilized in this analysis requiring 32 experiments, comprising of 16 factorial points, 10 axial points and 6 center points. The level of each was chosen based on the significance of the experiment. Based on the result of the procedure states considered, the level and variable studied are listed in Table1 below. A polynomial of the second degree by central composite design was produced to know the reaction as a basis of separable variables and their significance [9]. A statistical pattern following a second –order polynomial which comprises... Interaction terms was utilized to evaluate the prospect reaction. The reaction for the polynomial of the second degree is described below.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X^2{}_i + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j \quad (2)$$

Where Y is % methyl ester yield, xi and xj are the independent study factors(coded variables), and β_0 , $\beta_{i,}\beta_{ii}$ and β_{ij} are constant co-efficient, regression co-efficient of the linear terms, regression co-efficient of quadratic terms, and regression co-efficient of the interaction terms, respectively, and k is the number of factors studied and optimized in the experiment(number of independent variables). The Design– Expert 10.0.6.0 software package was used for regression analysis and analysis of variance (ANOVA).

Table 1. Experimental range and levels of the independent variables

Independent variable	**Units**	**Low level (-1)**	**High level (+1)**	**-α**	**+α**	**0 level**
Catalyst conc. (A)	Wt%	3(-1)	5(+1)	2(-2)	6(+2)	4
Methanol, (B)	Mol/mol	6(-1)	10(+1)	4(-2)	12(+2)	8
Temperature, (C)	°C	45(-1)	65(+1)	35(-2)	75(+2)	55
Reaction time (D)	Hours	3(-1)	5(+1)	2(-2)	6(+2)	4
Agitation speed (E)	Rpm	300(-1)	500(+1)	200(-2)	600(+2)	400

3.0. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

Scanning electron microscopic (SEM) analysis:The morphology of the thermally activated waste bone as shown in figure 1 (400x, and 2000x magnifications) comprises irregular size and shape particles. The smaller size of the grains and aggregates could provide higher specific surface areas.

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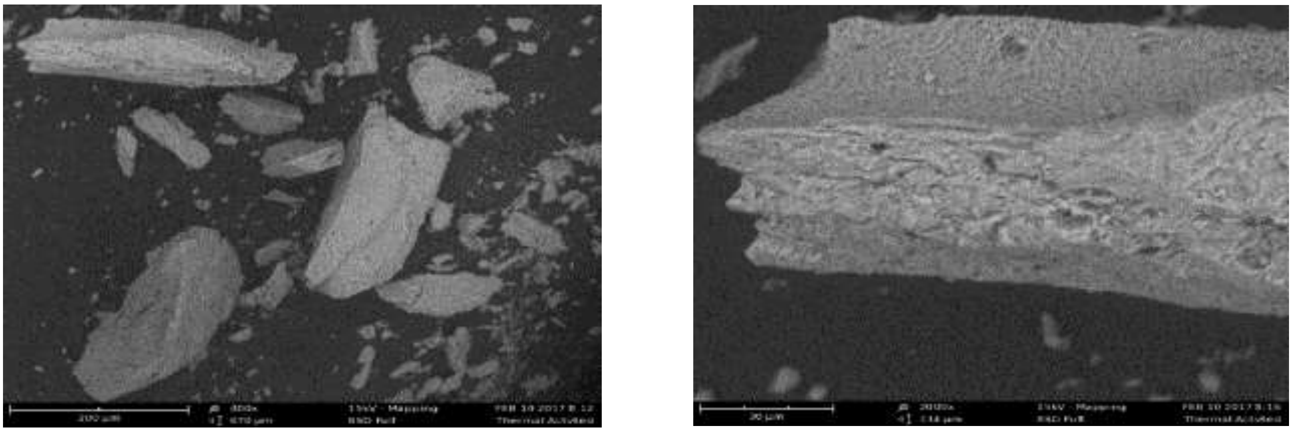

400 X 2000 X

Figure.1: SEM images of thermally activated waste bone at different magnifications (400x, and 2000x)

3.2. Fourier transform infrared spectrometer

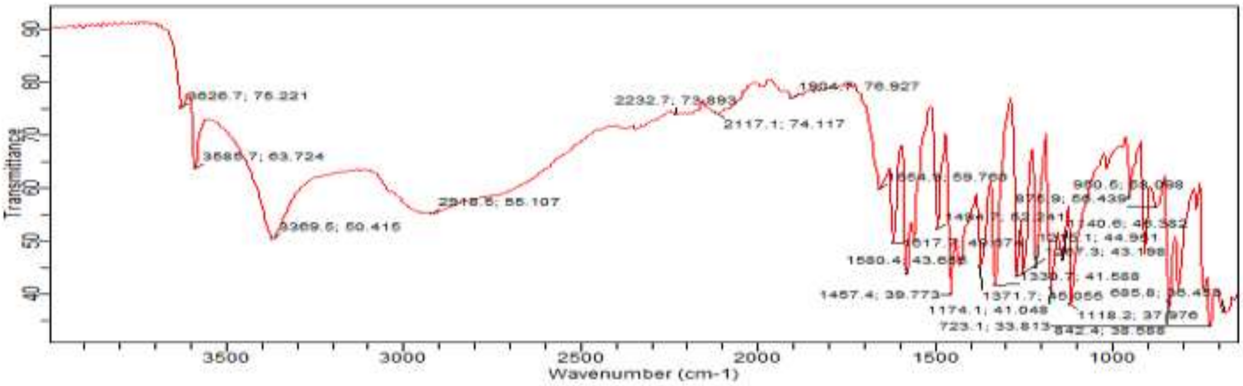

Figure.2. FTIR spectra of thermal activated waste bones

The FTIR of thermally activated waste bone is presented in figure 2. From the FTIR spectra it may be stated that all sample exhibit similar features in terms of bands position. However, remarkable differences exist regarding the intensity of bands. The weak bands from 1904.7 to 3369.7 cm^{-1} corresponds to aromatic rings. Bands at 3585.7 to 3627.7 cm^{-1} corresponds to hydroxyl group. The Sharp peaks at 1654.9 to 950 cm^{-1} corresponds to the PO_4^{3-} ions. The band at 1904.7 to 2232.7 cm^{-1} can be characteristic of C= C and O-H. The band at 2948.5 to 3369.5 cm^{-1} can be attributable to the molecule C = O. The bands around 842 to 685 cm^{-1} correspond to the vibrations of O-P-O bonds in calcium phosphate.

3.3. X-ray diffraction (XRD)

From figure 3, it is clear that the XRD pattern shows sharper peaks of 8^0,20^0,21^0 and 24^0 specifying good crystallinity. The peak positions for hydroxyapatite are in good agreement with the JCPDS (00-009-0432 and know influence specifying the appearance of contaminations was detected. Hence, quality HA with hexagonal structure was established. Therefore, the crystallite size of the catalyst was reduced. Thus, it indicates that crystallinity of the catalyst was reduced by thermal activation. [15]. It was also observed that the particle size reduction of the thermally activated waste bone spectra was topmost, showing high surface area, an imperative quality of a heterogeneous catalyst.

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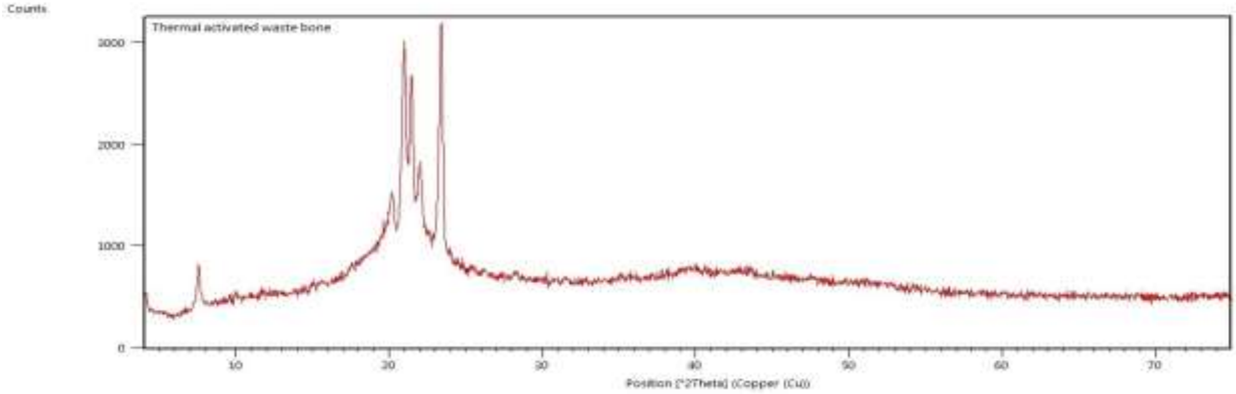

Figure 3. XRD pattern of activated waste bones

3.4. Thermogravimetric analysis (TGA) /Differential thermal analysis (DTA)

In figures 4, TGA analysis showed weight loss at temperatures between 100 to 200 and 300 to 400^{0}C due to dehydration of the precipitating complex and the loss of physically adsorbed water. Over a wide range of temperature 300 to 400^{0}C, the weight loss was mainly due to decomposition of organic matters. The increase in weight losses indicate the elimination of carbon to some degree in inclusion to water and gases. And low weight losses can be related to carbonate decomposition [5]. Beyond 400^{0}C and 450^{0}C, no essential weight loss was detected. Almost stable curve was noticed within this temperature range showing stage stability due to accomplishment of decomposition reaction and, liberation of bonded liquids and gases. The endothermic peak at temperature between 250 to 300^{0}C, also attributes to the degradation of organic substance and the decomposition of carbonate.

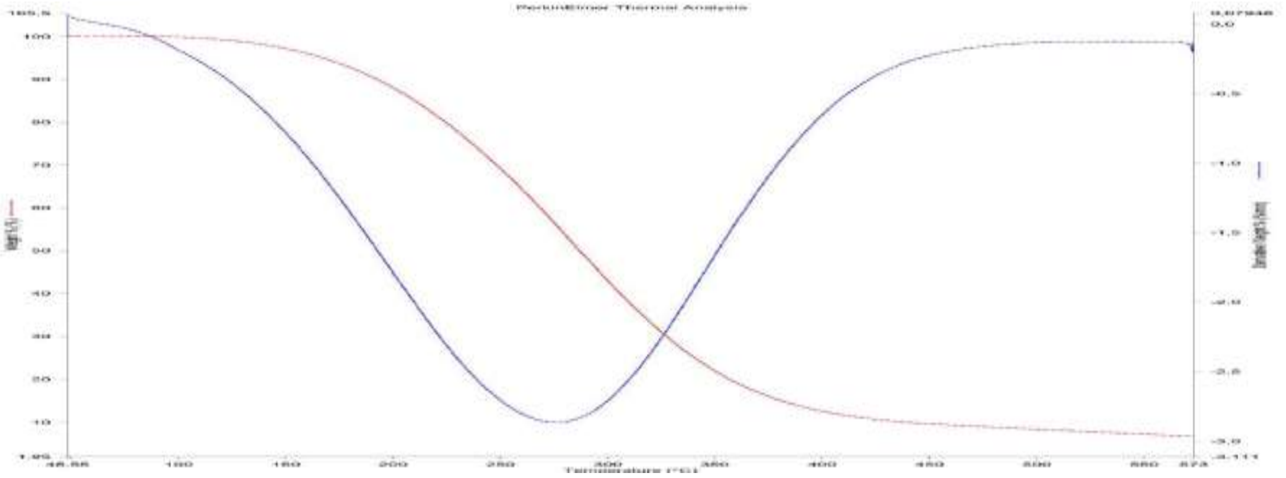

Figure 4. TGA/DTA thermogram of catalyst

3.5. Development of Regression Model

The five optimization process parameters of the transesterification of neemseed oil were investigated: catalyst concentration, methanol to molar ratio, temperature, reaction time and agitation speed. The sequential model sum of square and statistical summary of the neemseed oil transesterification using central composite design model is shown in Table 2. The highest order polynomial was selected from the model summary statistics, where the model is not aliased and additional terms are significant. The predicted R-squared of 0.9966 is in reasonable concurrence with the adjusted R-Squared value of 0.9904. Equation shows the resulted quadratic model in terms of coded factors. The model result of the investigational and predicted estimates of the percentage yield is shown in Table 2. The neemseed oil methyl ester yield ranged from 29% to 92% and experiments 1 and 29 (in standard order) gave the minimum and maximum yield. The Equation (3) 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 helpful for determining the relative impact of the factors by considering the factor coefficients.

$$Y= +89.48+1.08* A+3.75* B-0.25* C-0.67* D-3.50* E-1.88* AB-1.13* AC-4.25* AD+7.38* AE+3.75* BC-1.88* BD+1.75* BE+1.13* CD-2.00* CE+2.38* DE-9.23* A^2-10.10* B^2-6.85* C^2-4.35* D^2-8.98*E^2 \quad \text{-------------------} \quad (3)$$

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Where "Y" is the reaction, that is the transformation to methyl ester, and A, B, C, D and E shows the estimates of the trial/experimental changes: catalyst concentration, methanol to oil molar ratio, reaction temperature, reaction time and agitation speed. Positive sign in front of terms showed synergistic result in increased methyl ester yield while the negative sign showed antagonistic result which agrees with [7]. The model equation 4 showed that positive coefficients of linear and interaction terms A, B, AE, BC, BE, CD, and DE indicated to increase the FAME yield. Although, linear (C,D and E) , interaction (AB,AC,AD,BD and CE)and quadratic terms of (A^2,B^2,C^2,D^2 and D^2) had negative consequence that decrease the methyl ester yield. Hence, the model reduces to equation 4 after removing the inconsequential independent variables.

$$Y = 89.48+1.08* A+3.75* B+7.38* AE+3.75* BC+1.75* BE+1.13* CD+2.38* DE \text{ -------- } (4)$$

After elimination of insignificant model terms.

$$Y=89.48+3.75*B-3.50*E-4.25*AD+7.38*AE+3.75*BC-+2.38*DE-9.23*A^2-10.10*B^2-6.85*C^2-4.35*D^2-8.98*E^2 \quad -(5)$$

Table 2: Experimental design matrix for the factorial design

Run order	Catalyst conc. (wt %) A		Methanol/Oil molar ratio(mol) B		Temperature (oC) C		Time (Hours) D		Agitation Speed (Rpm) E		Yield (%)	Yield (%)
	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Exptal.	Pred.
1	-1	3.0	-1	6:1	-1	45.0	-1	3.0	+1	500.0	33.00	28.80
2	+1	5.0	-1	6:1	-1	45.0	-1	3.0	-1	300.0	63.00	56.72
3	-1	3.0	+1	10:1	-1	45.0	-1	3.0	-1	300.0	67.00	58.80
4	+1	5.0	+1	10:1	-1	45.0	-1	3.0	+1	500.0	73.00	63.72
5	-1	3.0	-1	6:1	+1	65.0	-1	3.0	-1	300.0	53.00	50.80
6	+1	5.0	-1	6:1	+1	65.0	-1	3.0	+1	500.0	47.00	43.72
7	-1	3.0	+1	10:1	+1	65.0	-1	3.0	+1	500.0	48.00	42.80
8	+1	5.0	+1	10:1	+1	65.0	-1	3.0	-1	300.0	67.00	59.72
9	-1	3.0	-1	6:1	-1	45.0	+1	5.0	-1	300.0	60.00	58.72
10	+1	5.0	-1	6:1	-1	45.0	+1	5.0	+1	500.0	60.00	56.63
11	-1	3.0	+1	10:1	-1	45.0	+1	5.0	+1	500.0	50.00	45.72
12	+1	5.0	+1	10:1	-1	45.0	+1	5.0	-1	300.0	40.00	32.63
13	-1	3.0	-1	6:1	+1	65.0	+1	5.0	+1	500.0	33.00	34.72
14	+1	5.0	-1	6:1	+1	65.0	+1	5.0	-1	300.0	40.00	39.63
15	-1	3.0	+1	10:1	+1	65.0	+1	5.0	-1	300.0	73.00	70.72
16	+1	5.0	+1	10:1	+1	65.0	+1	5.0	+1	500.0	60.00	55.63
17	-2	2.0	0	8:1	0	55.0	0	4.0	0	400.0	47.00	50.40
18	-1	6.0	0	8:1	0	55.0	0	4.0	0	400.0	44.00	54.73
19	0	4.0	0	4:1	0	55.0	0	4.0	0	400.0	42.00	41.57
20	0	4.0	+2	12:1	0	55.0	0	4.0	0	400.0	43.00	56.57
21	0	4.0	0	8:1	-2	35.0	0	4.0	0	400.0	50.00	62.57
22	0	4.0	0	8:1	+2	75.0	0	4.0	0	400.0	60.00	61.57
23	0	4.0	0	8:1	0	55.0	-2	2.0	0	400.0	60.00	73.40
24	0	4.0	0	8:1	0	55.0	+2	6.0	0	400.0	70.00	70.73
25	0	4.0	0	8:1	0	55.0	0	4.0	-2	200.0	53.00	60.57
26	0	4.0	0	8:1	0	55.0	0	4.0	+2	600.0	40.00	46.57
27	0	4.0	0	8:1	0	55.0	0	4.0	0	400.0	78.00	89.48
28	0	4.0	0	8:1	0	55.0	0	4.0	0	400.0	88.00	89.48
29	0	4.0	0	8:1	0	55.0	0	4.0	0	400.0	92.00	89.48
30	0	4.0	0	8:1	0	55.0	0	4.0	0	400.0	92.00	89.48
31	0	4.0	0	8:1	0	55.0	0	4.0	0	400.0	91.00	89.48
32	0	4.0	0	8:1	0	55.0	0	4.0	0	400.0	89.00	89.48

3.6. Analysis of Variance (ANOVA) for model regression

Design Expert Software Version 10.0.6.0 was used to develop a quadratic model. Further, summary of Analysis of variance (ANOVA) technique was used to evaluate how good the model fits.

Table 3.Analysis of variance (ANOVA) for model regression

Source	Coefficient estimate	Degree of freedom	Sum of square	Mean squares	F-value	P-value (Prob >F)
Model	**89.48**	**9967.98**	**9967.98**	**498.40**	**160.14**	**< 0.0001 significant**
A	1.08	28.17	28.17	28.17	9.05	0.0119
B	3.75	337.50	337.50	337.50	108.44	< 0.0001
C	-0.25	1.50	1.50	1.50	0.48	0.5019
D	-0.67	10.67	10.67	10.67	3.43	0.0911
E	-3.50	294.00	294.00	294.00	94.47	< 0.0001
AB	-1.88	56.25	56.25	56.25	18.07	0.0014
AC	-1.13	20.25	20.25	20.25	6.51	0.0270
AD	-4.25	289.00	289.00	289.00	92.86	< 0.0001
AE	7.38	870.25	870.25	870.25	279.62	< 0.0001
BC	3.75	225.00	225.00	225.00	72.29	< 0.0001
BD	-1.88	56.25	56.25	56.25	18.07	0.0014
BE	1.75	49.00	49.00	49.00	15.74	0.0022
CD	1.13	20.25	20.25	20.25	6.51	0.0270
CE	-2.00	64.00	64.00	64.00	20.56	0.0009
DE	2.38	90.25	90.25	90.25	29.00	0.0002
A^2	-9.23	2497.52	2497.52	2497.52	802.48	< 0.0001
B^2	-10.10	2993.64	2993.64	2993.64	961.89	< 0.0001
C^2	-6.85	1377.31	1377.31	1377.31	442.54	< 0.0001
D^2	-4.35	555.64	555.64	555.64	178.53	< 0.0001
E^2	-8.98	2364.02	2364.02	2364.02	759.58	< 0.0001
Residual		34.23	34.23	3.11		
Lack of fit		4.90	4.90	0.82	0.14	0.9838 Not significant
Pure error		29.33	29.33	5.87		
Cor Total		10002.22	10002.22			

Std. Dev. =1.76, Mean = 59.84, C.V. % =2.95, PRESS =154.17, R-Squared =0.9966,
Adj R-Squared =0.9904, Pred R-Squared = 0.9846 Adeq Precision =42.458.

From Table 3, it may be observed that the model F-value of 160.14 with p-value of <0.0001 suggests the model is significant. The value of P<0.0001 shows that there is only a 0.01% chance that the F-value could occur due to noise. P-values < 0.05 indicate that the model terms are significant [12].In this case, linear terms B(methanol to oil ratio),E(agitation speed),interaction effect of AD(catalyst concentration with reaction time),AE(catalyst concentration with agitation speed),BC(methanol to oil molar ratio with temperature),DE(reaction time with agitation speed),A^2(quadratic effect of catalyst concentration),B^2(quadratic effect of methanol to oil molar ratio),C2(quadratic effect of temperature),D^2(quadratic effect of reaction time) and E^2(quadratic effect of agitation speed) have significant effect (significant model terms) on neemseed methyl ester catalyzed by thermal activated waste bone. The insignificant model terms were removed and may result in an improved model. The model reduced to equation 4.9. The relationship between predicted and experimental biodiesel yield is shown in figure 6. It can be seen that there is high correlation (R-squared value = 0.9966) between the predicted and experimental methyl ester yield. The predicted estimated and experimental estimates were in reasonable agreement (R-squared value close to unity), indicating the good fitness/adequacy of the model.

High values of predicted R^2 (0.9846) and adjusted coefficient of determination (R^2-Adj:0.9904) and low value of coefficient of variation (C.V) (2.95%), showed precision of fitted model. That is better reliability of the fitted model [7,13]. A ratio greater than

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4 is desirable. The Adeq. precision value of 42.458 which measures the noise to signal ratio showed a sufficient signal. This analysis was further examined using the normal probability plot of the residuals and the predicted residuals plot as shown in figure 5 and 6, respectively. The normal probability plot of the residuals and predicted versus actual plot showed that the inadequacies are scattered conventionally in an undeviating line and are inconsequential.

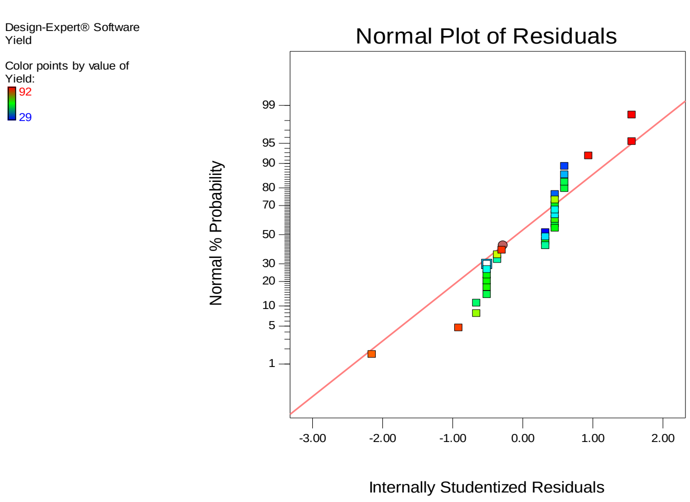

Figure 5. Normal Probability plot of residuals yield (%)

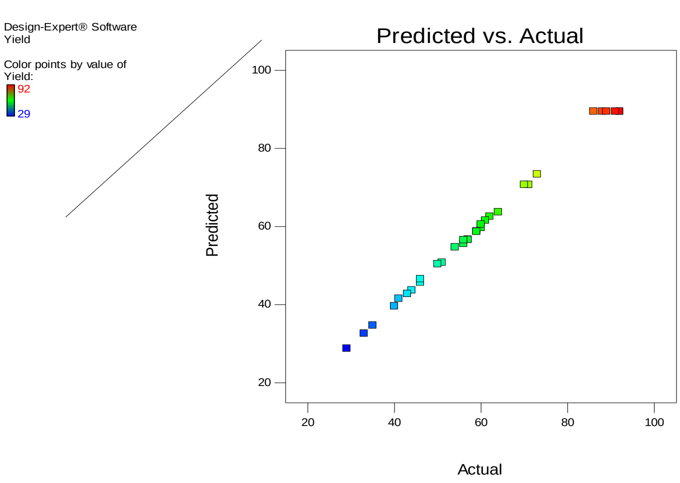

Figure 6. Predicted biodiesel yield (%) versus Experimental yield (%)

3.7. Interaction between the independent variables (3D response surface plots)

The results of the procedure variables on the methyl ester transformation were examined by plotting three-dimensional surface curves against any two unconventional variables while keeping the other variables at their central (0) level [10]. The 3D plots of the reaction from the result of independent variables are shown below.

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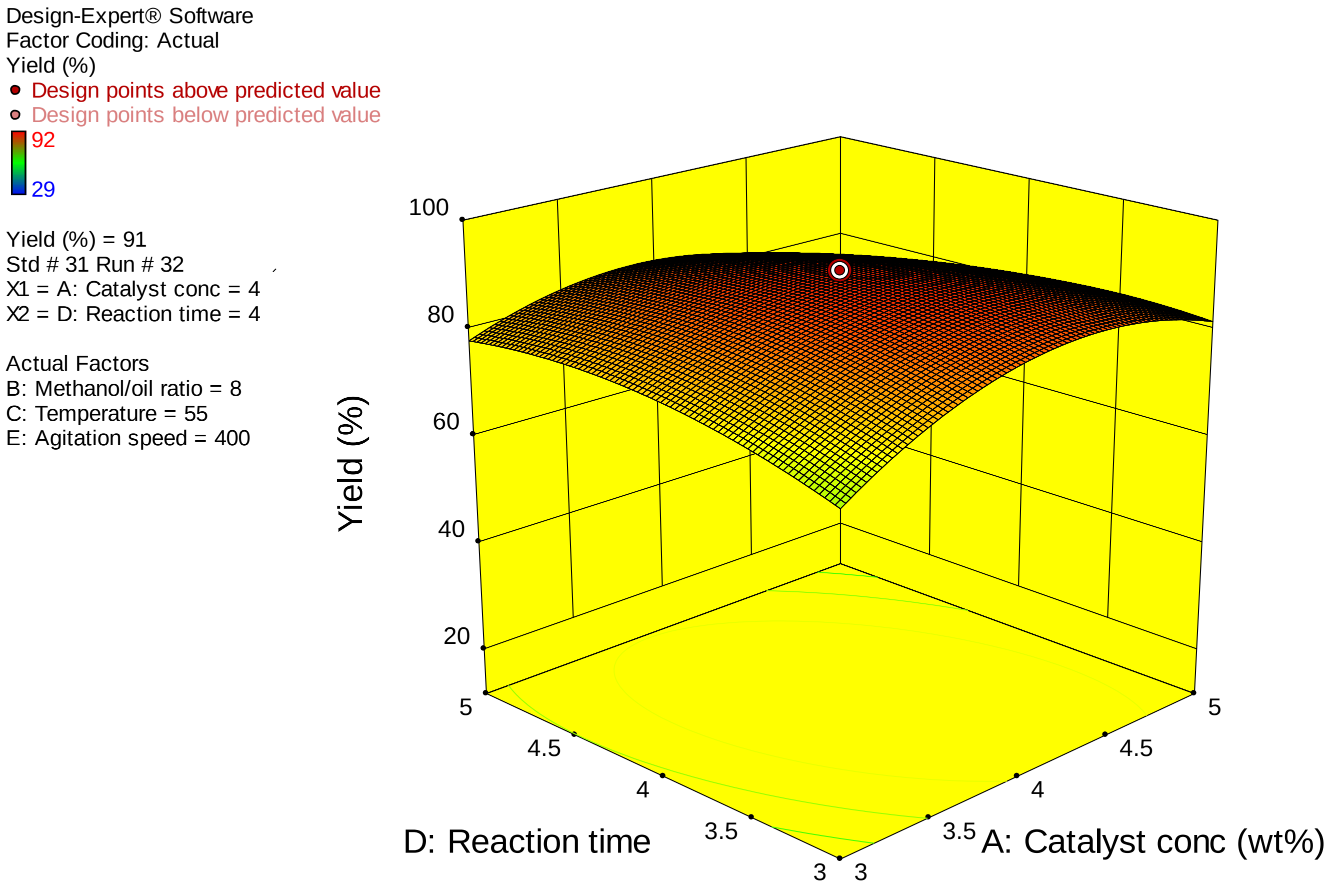

Figure7.3D response surface plot of the interaction effect of catalyst concentration and reaction time on biodiesel yield

The 3D reaction plot in figure 7 shows that there is a consequential interconnection of catalyst weight (%) and reaction time . The three dimensional response surface plot showed increase in response time and catalyst weight which leads to a corresponding increase in yield. The increase of catalyst weight gave rise to significant increase in methyl ester yield at low reaction time. Though, the methyl ester yield was moderately infuenced by the increase of catalyst at high reaction time. From the plot ,it was seen that the yield became stable when there was further increase.

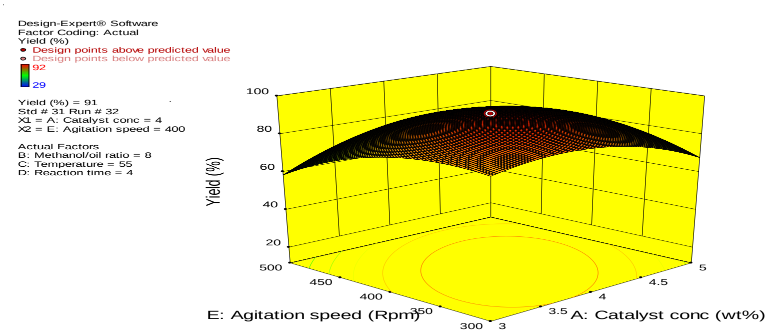

Figure 8.3D response surface plot of the interaction effect of catalyst concentration and agitation speed on biodiesel yield

The 3D plot revealed the intraction result of catalyst concentration and agititation speed. The plot showed that rise in catalyst concentration and agitation speed has useful result on methyl ester yield to certain point. That is increase in catalyst concentration and agitation speed up to 4wt% and 400rpm,respectively, increase the yield of biodiesel.Excessive mixing reduces the yield of biodiesel.

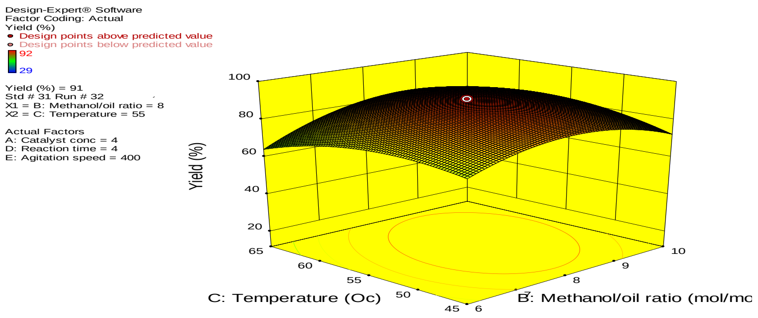

Figure 9.3D response surface plot of the interaction effect of methanol to oil ratio and temperature

Figure 9 showed the interactive result of methanol/oil ratio and temperature. From the 3D plot, it showed that the highest yield (92%) was obtained at temperature of 55°C and methanol/oil ratio of 8:1. As the temperature rises, the solubility of methanol in the oil rises and so does the speed of response.Conversely,an extreme quantity of alcohol above 8:1 makes the recovery of glycerol difficult.

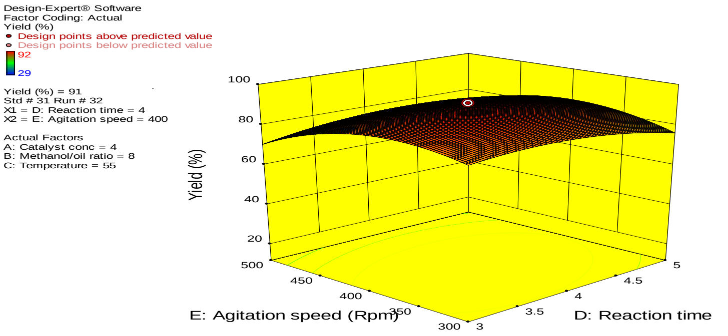

Figure 10.3D response surface plot of the interaction effect reaction time and agitation speed

Figure 10 shows the interactive result of reaction time and agitation speed. From the plot, methyl ester yield increased significantly with increase in reaction time and stir speed until a decrease in yield above 4 hours and 400 rpm. This may be due to excessive agitation. Excessive agitation causes splashing and the mixture tend to foam which may result in cavitation corrosion.

3.8.Validation of the Optimization result

The states with the highest methyl ester yield were selected for further validation. Trials were run to confirm the correctness of the predicted model. The optimal conditions for the highest value of biodiesel transformation are as follows: 4wt% catalyst concentration, 8:1 methanol to oil molar ratio, 4hours of reaction time, 55^{0}C of reaction temperature and 400rpm of agitation speed. The optimal (predicted) biodiesel yield of 91.2% was obtained. Comparing the experimental and predicted results as shown in table 4, it can be seen that the error between the experimental and predicted are close. This means that the experimental value obtained is reasonably close to the predicted value calculated from the model with relative small percentage error (0.8%). This showed that the regression model was satisfactory.

Table 4. Results of the model validation at optimum conditions

Cat.Conc.(wt%) **A**	**Methanol/oil ratio (mol/mol.)** **B**	**Tempt.(oC)** **C**	**Time(hr)** **D**	**Speed (rpm)** **E**	**Exptal. Yield (%)**	**Pred.yield (%)**	**Percentage error (%)**
4	8	55	4	400	92.00	91.2	0.8

4.0. CONCLUSION

Response surface methodology with central composite design was efficiently utilized in examining the results of different variables and optimization of methyl ester production. The best process parameters for methyl ester production are catalyst concentration of 4wt%, methanol to oil molar ratio of 8:1, reaction temperature of 55°C, reaction time of 4h, and agitation speed of 400rpm.The optimum yield of biodiesel was found to be 92.0%. The results prove that the calcium oxide catalyst derived from waste of animal bone had excellent activity during transesterification reaction. On the basis of ANOVA, methanol/oil ratio and agitation speed had a significant effect on NSOB yield. Further trial was carried to verify the best states obtained and this showed that the predicted values were in agreement with the experimental values. Conclusively, the procedure variables of optimization using response surface methodology with central composite design provides best/improved biodiesel yields with neemseed oil.

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