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Modeling and optimization of lucky nut biodiesel production from lucky nut seed by pearl spar catalysed transesterification

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Abstract

In 2015, the Worldatlas recorded 50 countries whose source of income is fossil fuel and its derivatives. Surprisingly, these countries solely depend on this source of energy up to 100% (Omar, Qatar, Kuwait and Saudi Arabia) because of technology improvement. It's so sadden that apart from its adverse effect on the economics of the countries, fossil fuels harmful effects on the universe cannot be overlooked. Meanwhile, the use of renewable energy as a replacement for fossil fuel and its derivatives are faced by the high oil price, high cost of investment for alternative energy, and unfathomed electricity prices. This research work evaluates desirability of making use of alternative source of energy sources by making use of biomass oil over the use of fossil fuel and its derivatives for electricity generation.

Lucky nut is an agricultural non edible seed that was employed as raw material for biofuel production. The non-edible oil was extracted from the seeds and the oil was further converted to Lucky nut biofuel via a heterogeneous based catalyst produced from calcinated pearl spar. For modelling and optimization, design expert coupled with genetic algorithms were used to generate experimental designs so as to correlate the variable factors considered for production.

The extraction of Lucky nut seed revealed the optimum production yield of 50.80% (v/v) and the oil is highly unsaturated. Energy Dispersive X-ray Fluorescence Spectrophotometer analyses and scanning electron microscope (SEM) of the calcined catalyst obtained from pearl spar showed the major component found in the pearl spar was K with relative abundance of 58.48%, which favoured the yield of Lucky nut biodiesel (91.00% (v/v)). Based on predicted values, the optimum validated Lucky nut biodiesel by RSMED and ANNED were 89.68% (v/v) and 92.87% (v/v), respectively. Produced properties of biofuel conformed to the biofuel standard.

The study concluded that Lucky nut seed is a good source of oil, and its transformation to alternative fuel via a using calcined catalyst proved its fitness as a replacement for fossil fuel.

Keyword: Chemical engineering

1. Background

Coal, natural gas and oil are source of energy formed over billions of ages from the decay of plants and animals. These assets are entirely irreplaceable ever since the world formed. Also, the exploitation of the use of burning fuels cause pollution to the water we drink, air we breathe, and the soil for agricultural purposes. This in turn, affects humanity, vegetation, wildlife, and the natural world. The outcomes are destruction of wildlife and vegetation, as well as sicknesses, birth defects, and death.

According to Worldatlas, 2015 reports, currently, there are at least over 34 countries whose sources of their income were totally based on the use of coal, natural gas and oil for their respective energy needs. Other countries, like Nigeria depend on these for their energy needs. Therefore, there is an urgent awareness policy to inform their populace on the danger posed by use of coal, natural gas and oil on the rest of the countries and change of energy sources to include new renewable means such as biofuel.

Biofuel, fuel derived from biomass material has bloomed as renewable source of fossil fuel, which is produced through modern biological routes [1, 2]. Biofuel can be said to be an alternative to conventional diesel which is transformed from vegetable seed oils mixed with −OH group in the presence of a based catalyst [3].

However, the use of most vegetable oils for biofuel production is not viable, due of food shortage pressures and greater costs production needed. Thus, the use of biomass oil could serve as substitute to overawe the challenges of food shortage pressures and larger production cost [2].

Lucky nut has bloomed as biomass source of derivative for alternative diesel manufacture. The tree is an evergreen tropical shrub with needle like leaves usually greenish in colour (Fig. 1). Usually surrounded by waxy coating to minimize dehydration, with it stem usually changed in colour as it grow older. The seed mainly called lucky nut seeds contain high percentage oil, ranging from 33.0 to 77. 62% (v/v) which are used for biofuel production [4, 5].

Rudeolf Diesel has demonstrated the use of oil in an engine, but owing to it highly viscous, incomplete ignition, unwanted particulate substances and low volatility, it cannot suitably work like a conventional diesel in a modern engine designed for modern fuel, [6]. Therefore, various techniques such as pyrolysis, microemulsion and transesterification via catalytic conversion have been applied to overcome these problems [7, 8, 9]. However, transesterification techniques have been established to be highly effective, time-saving and economical among other [10].

Complete seeds   **Seeds without flesh**

Fruit seeds   **Milled seed powder**

Fig. 1. Lucky nut.

Meanwhile, catalytic conversion of oil to biofuel could entail the use of homogeneous (NaOH/KOH) or heterogeneous (derived from solid materials) catalysts [11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. The major shortcomings when homogeneous catalysts are used in production of biofuel are the problems recycling from the products and related problems which can lead to soapy formation, high oil and −OH required, health effects and cost required to purify the products [21].

Response surface methodology experimental design (RSMED) is design expert software that can easily handle data analysis and has been used effectively in modeling and optimizing biodiesel production. The benefits of this software over others include availability, asset in statistical quality control, expressive and inferential statistics, statistical process control (SPC), reliability, gage repeatability and reproducibility (GR&R) studies, process ability and improved graphing output [22]. Artificial neural network experimental design (ANNED) is an educative based on assessment method, which shows a nonlinear relationship with joining factors and product formation thru reiteration of outcomes acquired from experimental design [23]. ANNED has showed to be enhanced design software in terms of data fitting and prediction when applied in educational or health fields [24, 25, 26, 27]. These software's and others have been applied either in single or combination form to model and optimize the experimental factors so as to determine the optimum yields [28, 29, 30, 31, 32, 33, 34, 35, 36].

In this research work, Lucky nut seedoil was explored to produce biodiesel via heterogeneous base catalyst produced from activated calcined pearl spar. For modelling and optimization, RSMED and ANNED were employed so as to generate the number of experimental runs, determine the predicted yield, compare the error values, and analyze the various variable factors responsible for optimum production of biofuel and increasing the process efficiency. Lastly, the fuel properties of Lucky nut oil biodiesel were evaluated with a view to determining its suitability in replacing fossil fuels.

2. Materials and methods

2.1. Materials

Lucky nut was harvested from Onna Stadium, Onna L.G.A. in Akwa Ibom, Nigeria (Fig. 1). The nut was dried in the sun for 15 days until it achieve a bone dried weight, the kernel fruits were manually shelled and the fruits were further dried in an oven for 4 h at temperature of 65 °C. Separation of the chaff from the fruit was carried out by sorting before crushing into fine powder prior to extraction.

Pearl spar, a white spar, identified as grade 11 having coverage of $70.00 \, kg/m^2$, were collected from Ibom Plaza garden in Uyo, Akwa Ibom State. Washing was carried

out to remove unwanted materials, dried for one hour at 100 °C before grind to lower particle size for easy activation (Fig. 2). All chemicals used were of standard grade and needed no further purification.

2.2. Methods

2.2.1. Method of oil extraction from Lucky nut powder

Based on experimental runs by RSM, the powdered sample was weighed and placed in the extractor through the muslin cloth. N-hexane was used as organic solvent for extraction. Box behnken design with 3-factors generated seventeen (17) experimental runs; these runs were carried out by varying the design factors in the Soxhlet extractor. The excess n-hexane was removed using rotary evaporator, and the oil yield was computed using Eq. (1).

$$Lucky \ nut \ oil \ yield \ (Ctoy) \ (\%) = \frac{weight \ of \ \text{oil}}{weight \ powder} \tag{1}$$

2.2.2. Design of experiment: extraction of oil from Lucky nut powder

To design experiment for oil extraction from lucky nut powder, three independent variable factors were careful considered, since 2^n (where n = 3) full factors design

Pearl Spar   **Grind Pearl Spar**

Powdered Pearl Spar for calcination   **Calcined Pearl Spar for analysis**
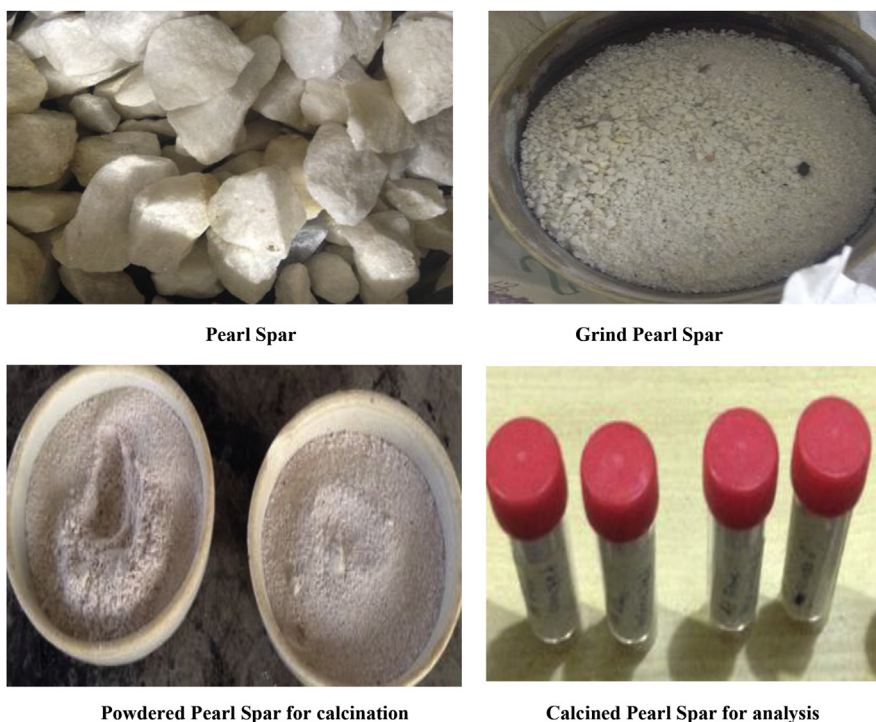
Fig. 2. Pearl spar.

and central composite design will give 20 experimental runs [14, 37]. In order to reduce the number of experimental runs, Box-Behnken Design (BBD$_{RSM}$) was employed which generated seventeen experimental runs used to study the effects of selected factors on oil yield. Table 1 showed the selected factors such as sample weight: X_1, extraction time: X_2, solvent volume: X_3 and their levels. For the coefficient of the quadratic model of the response fitting, multiple regressions model was adopted using SEDE. 11.0.4 x86/x64. Regression analysis and test of significance are the computational exhaustive route that is best carried out via statistical software; hence the quality of the fitted model was estimated using test of significance and regression analysis of variance (ANOVA) via Eq. (2).

$$R_F = \tau_0 + \sum_{i=1}^{k} \tau_i X_i + \sum_{i=1}^{k} \tau_{ii} X_i^2 + \sum_{i<j}^{k} \tau_{ij} X_i X_j + e \qquad (2)$$

With RF is the experimental value, τ_0 is the intercept term, τ_i are the coefficient terms for linear τ_{ii}, quadratic τ_{ij} and interaction i, j is the selected factors, $= 1, 2, 3$.

2.2.3. Physicochemical characteristics of Lucky nut oil

The characteristics of the Lucky nut oil were evaluated using standard [38] official methods of analysis and Wij's iodine method [10] as described below.

Oil sample of 0.26 g was dissolve in 10 ml of cyclohexane, and 20 ml of Wij's was mixed together in a 250 ml beaker, the cork beaker was kept in a dark place for half an hour, 20 ml of 10% potassium iodide solution was then added. The resulting mixture was then titrated with 0.1 M $Na_2S_2O_3$ using two drops of starch as indicator. Iodine value was calculated using Eq. (3).

Table 1. Variable factors considered for lucky seed oil extraction and transesterification of lucky seed oil to biofuel.

Variable	Symbol	Coded factor levels		
		−1	0	+1
Lucky seed oil extraction				
Sample weight (g)	X_1	45	55	65
Extraction time (min)	X_2	45	50	55
Solvent volume (ml)	X_3	220	245	265
Transesterification of lucky seed oil to biofuel				
Reaction time (min)	X_1	50	60	70
Methanol/oil ratio (v/v)	X_2	0.15	0.20	0.25
Catalyst amount (g)	X_3	2.50	4.00	5.50

$$Iodine\ Value = \frac{[\rho_o - \rho]\ X\ MX12.69}{0.26} \qquad (3)$$

With M = Concentration of sodium thiosulphate used; ρ_o = Volume of sodium thiosulphate used as blank; ρ = Volume of sodium thiosulphate used for determination.

2.2.4. GCMS analysis of Lucky nut oil

To determine the acid composition of the extracted oil, an Agilent 19091S-433HP-5MS GCMX was used. The operating conditions of the equipment were as described by [4] with no modification.

2.3. Elemental characterization of calcination catalysts

Four (4) samples (Fig. 2), each weighing 100 g of the grinned pearl spar were prepared. Two (2) samples were saturated in CH_3OH for 20 min, stirred rigorously before filtered. The filtrate was discarded, while the residual cake and the two (2) samples not soaked in methanol were calcined in an oven furnace at 700 °C for 5−6 h, respectively.

To ascertain the calcined Pearl Spar with high abundant of base catalyst, EDXRF Spectrophotometer (EDX3600B) was used to determine the relative abundance of each element present. The EDXRF Spectrophotometer was standardized with group II element (silver), the analysis was performed using ore standard calibration curve. Furthermore, an electron microscopy (SEM) was used to determine the position of the activated catalysts. The calcined pearl spar identified with the high abundant base catalyst was use for the based catalysed transesterification of biofuel production.

2.4. The production of biofuel from Lucky nut oil

2.4.1. Acid catalysed: esterification process (reducing % FFA)

In order to minimize the challenges posed by the high extracted oil free fatty acid, H_2SO_4 was used follow the modified method of [39]. 100 ml of the oil was measured in a three necked reactor, preheated on a hot plate with magnetic stirrer. A known volume of acid (H_2SO_4) with a known volume methanol were mixed separately, before the resulting mixture was transferred to the pre-heated oil placed on hot plate, allowed to stir continuously for 1 h to produced esterified oil. After 1 hr, the esterified oil was separated from by product (CH_3OH) using separating funnel. Surplus CH_3OH in the esterified oil was evaporated preceding the determination of the acid value. The acid value of oil was determined using the standard method of AOAC, 1997. These steps were carried out repeatedly under different

conditions of the mixture of H_2SO_4 and methanol until the minimum acid value was obtained.

2.4.2. Base-catalysed transesterification of esterified oil

Biodiesel production was established using transesterification of the oil already esterified using the modified method of [36] was adopted. A known volume of the oil with reduced FFA was measured into a 500 ml reactor, a know prepared catalyst pearl spar was weighed and dissolved in a known CH_3OH in a separate flask. The flask was placed on a hot plate equiped with magnetic stirrer with adjustable temperature control (60 °C), and the reaction was completed at designated time. At the end of the reaction, the products were set to stand in a separating funnel for 2 days to allowed glycerol -biofuel gravity settling. The glycerol settled at the bottom of the flask was flowed out, leaving behind biofuel in the funnel. Since the purity of the biofuel determines the fuel properties, the biofuel left in the funnel was then washed with ionized water until the biofuel was purely achieved. The neat biodiesel was tapped into a conical flask, where it was further dried over heated potassium chloride. The cleaned, dried biodiesel was then filtered, and the biodiesel volume was evaluated as % (v/v) (Eq. (4)). The procedure was repeated for other experimental runs.

$$Biodiesel\ yield\ \%(v/v) = \frac{Volume\ of\ biodiesel\ produced}{Volume\ of\ esterified\ oil} \tag{4}$$

2.5. Design of experiments for biodiesel production

A total of 17 experimental runs were performed in order to optimize the production of biodiesel from the low FFA oil. Selected variable considered were reaction time in min represented by X_1; methanol/oil ratio represented by X_2, and catalyst amount in g represented in X_3 as showed in Table 1. The effects of the variables were randomized so as to reduce the unwanted impact of unexpected variability in the experimental yield. Meanwhile, second order quadratic model was used for the process. To compare the experimental value to the selected variables, multiple regressions were used to fit the coefficients of the second-order quadratic polynomial model of the response. The quality of the fit of the model was evaluated using both test of significance and analysis of variance (ANOVA) analysis.

2.6. Model testing and estimation

To determine the correlation among the selected variables and the responses, a simple linear regression must be satisfied. The connection between the oil/biodiesel and the selected factors under consideration are expressed by Eq. (2). Meanwhile, Eqs. (5), (6), (7), and (8) were used for model testing and estimation capabilities.

These values were used together to compare the BBD_{RSM} and ANN_{GA} models by comparing the evaluated values for the models [39].

$$ADD = \left\{ \frac{1}{n} \left| \sum_{i=1}^{n} \left(\frac{\varnothing_{i,exp} - \varnothing_{i,cal}}{\varnothing_{i,exp}} \right) \right| \right\} \tag{5}$$

$$RMSE = \sqrt{\frac{\sum \left(\varnothing_{i,cal} - \varnothing_{i,\exp} \right)}{\rho}} \tag{6}$$

$$R^2 = 1 - \sum_{i=1}^{n} \frac{\left(\varnothing_{i,cal} - \varnothing_{i,exp} \right)^2}{\left(\varnothing_{avg,exp} - \varnothing_{i,exp} \right)^2} \tag{7}$$

$$\overline{R}^2 = 1 - \left(1 - R^2 \right) \left[\frac{\rho - 1}{\rho - (\varnothing + 1)} \right] \tag{8}$$

with the number of observed data/sample size is ρ, $\varnothing_{i,exp}$ is the experimental value, $\varnothing_{i,cal}$ is the calculated value and $\varnothing_{avg,exp}$ is the average experimental value, $\varnothing$ is the number of independent variables in the regression analysis. AAD is the absolute average deviation, RMSE is the root mean square error, R^2 is the coefficient of determination and is the adjusted coefficient of determination.

2.7. Properties of biodiesel

2.7.1. Physicochemical properties of biodiesel

It is necessary to determine the properties of the biofuel produced from the Lucky nut seed so as to ascertain its suitability for running an internal combustion engine. Properties of the biodiesel like physical, chemical and fuel properties were determined and recorded using standard methods.

2.7.2. Fuel properties of the biodiesel

To ascertain the qualities of the biodiesel produced, the fuel properties must be estimated using standard ASTM 2015 methods stated in Eqs. (9), (10), (11), (12), and (13).

$$CN = 46.3 + \frac{5458}{SV} - 0.225 \, IV \tag{9}$$

$$HHV \, (\text{MJ/kg}) = 49.43 - [0.041(SV) + 0.015(IV)] \tag{10}$$

$$API = \frac{141.5}{SG@15\,°C} - 131.5 \tag{11}$$

$$DI = \frac{CN - 10}{0.72} \tag{12}$$

$$AP = \frac{100DI}{API} \tag{13}$$

with CN is the Cetane Number, HHV is the higher heating value, API is the American petroleum institute, DI is the diesel index, AP is the aniline point, SV is the saponification value, IV is the iodine value.

3. Results and discussion

3.1. Modeling and optimization: oil extraction

Table 2 shows the number of experimental runs expressed in coded form, the results of the experimental carried out, the predicted values by both RSM and ANN and the residual values obtained. It was observed from the table that the experimental highest oil obtained was 53.00% (w/w) at coded values of $X_1 = 0$, $X_2 = -1$ and $X_3 = 1$. However, statistical analysis via RSM predicted 47.6935% (w/w) at $X_1 = -0.5460$, $X_2 = -1.0000$ and $X_3 = 0.0608$ and ANN predicted 52.95%

Table 2. Coded factors with experimental oil results, predicted and residual values by RSM and ANN for Oil extraction.

Std. run	X_1	X_2	X_3	*Oil* % (v/v)	Predicted		Residual	
					RSM	ANN	RSM	ANN
1	−1.000	−1.000	0.000	46.2	46.09	46.20	0.1125	3.5527E-14
2	1.000	−1.000	0.000	50	49.71	49.1	0.2875	7.1054E-15
3	−1.000	1.000	0.000	45	45.05	45	−0.0500	1.4211E-14
4	1.000	1.000	0.000	44	44.11	44	−0.1125	7.1054E-15
5	−1.000	0.000	−1.000	45	45.29	45	−0.2875	7.1054E-15
6	1.000	0.000	−1.000	45	46.95	45	0.0500	7.1054E-15
7	−1.000	0.000	1.000	47	47.40	47	−1.40	7.1054E-15
8	1.000	0.000	1.000	49.1	49.23	49.1	−0.1250	7.1054E-15
9	0.000	−1.000	−1.000	43.6	43.84	43.6	−0.2375	1.9185E-13
10	0.000	1.000	−1.000	47	47.40	47	0.6000	0
11	0.000	−1.000	1.000	53	53.16	53	−0.1625	1.8474E-13
12	0.000	1.000	1.000	44	43.76	44	0.2375	7.1054E-15
13	0.000	0.000	0.000	46	46.84	47.4	0.1625	1.4
14	0.000	0.000	0.000	48.5	47.40	47.4	1.10	1.1
15	0.000	0.000	0.000	49.5	47.40	47.4	2.10	2.1
16	0.000	0.000	0.000	48	47.40	47.4	0.6000	0.6
17	0.000	0.000	0.000	45	44.88	45	0.1250	7.1054E-15

Table 3. Test of significance for regression coefficient.

Source	SS	df	MS	F-value	P-value
X_1	3.00	1	3.00	1.49	0.2616
X_2	20.48	1	20.48	10.17	0.0153
X_3	19.58	1	19.58	9.70	0.0170
X_1^2	2.29	1	2.29	1.14	0.3216
X_2^2	0.5533	1	0.5533	0.2748	0.6163
X_3^2	0.0796	1	0.0796	0.0395	0.8480
X_1X_2	5.76	1	5.76	2.86	0.1346
X_1X_3	1.10	1	1.10	0.5476	0.4834
X_2X_3	38.44	1	38.44	19.09	0.0033

(w/w) at variable factors of $X_1 = 0.11$, $X_2 = 1.00$ and $X_3 = 0.52$, respectively. Based on predicted values, the experiment was carried out in triplicates so as to validate the values at different variable conditions predicted by RSM and ANN. An average of oil of 46.82% (w/w) and 50.80% (w/w) were obtained for RSM and ANN, respectively. Table 3 showed the results of the test of significance for every regression coefficient, it was observed that the p-values of X_2, X_3, and X_2X_3 were the most significant model terms with $p < 0.05$.

A higher F-value signifies a well-fitting of the RSM model to the experimental data [41]. According to [42], an F-value along with low p-value indicates a high significance of the regression model. Nevertheless, the p-value should be lower than 0.05 for the model to be statistically significant [43]. Based on these reports, the regression model found in Table 4 was highly significant, as it is evident by the F-value = 5.50 and the low p-values = 0.0221, respectively.

To test the fit of the model equation, the regression model was established using R^2 as an estimation of how much variability in the observed response values can be explained by the experimental factors and their interactions [44]. The R^2 value is

Table 4. Analysis of variance (ANOVA) of regression equation.

Source	SS	df	MS	F-value	P-value
Model	91.45	9	10.16	5.05	0.0221
Residual	14.09	7	2.01		
Lack of fit	0.3925	3	0.1308	0.0382	0.9886
Pure error	13.70	4	3.42		
Cor. total	105.54	16			

RSM: $R^2 = 86.65\%$, R^2 (adjusted) $= 69.48\%$, R^2 (predicted) $= 73.77\%$
ANN: $R^2 = 93.28\%$, R^2 (adjusted) $= 87.02\%$, R^2 (predicted) $= 92.53\%$

Where: df = Degree of Freedom, MS = Means Square, SS = Sum of Square, F = Fischer, P = Probability.

always between 0 and 100% [12, 45]. However, to create a fitted model, R^2 should at least 80% [46]. The R^2 value of 86.65% recorded in Table 5, which leaves only 13.35% of the variability not explains by observed response, indicated that an unexplainable total variation which can be caused by other variables excluded from the model parameter.

Table 5 contained the results of analysis of variance of the regression equation model. The mathematical expression of the relationship between oil yield and the variables considered for oil extraction is given in Eq. (14). All negative values have reduction impact on the oil and positive values have ability to increase the yield.

$$Oil/Cto\,\%(v/v) = +47.50 + 0.6125X_1 - 0.160X_2 + 1.56X_3 - 0.7375X_1^2$$
$$- 0.3625X_2^2 - 0.1375X_3^2 - 1.20X_1X_2 - 0.110X_1X_3$$
$$+ 0.5250\,X_2X_3 \tag{14}$$

The relationship between the variables and the response can be represented on graphical drawing, placing the experimental levels of each variable on the one side, and the type of interactions between the test variables, on the other, which allows deducing the optimum conditions. Figs. 3 and 4 therefore shows the contour and 3 dimensional surface plots for oil extraction from oil seed under the viable optimum conditions for RSM and ANN. Meanwhile, the line graph helps to determine the relationship between two sets of values, with one data set always being dependent on the other set. Fig. 5 therefore shows a plot predicted against the experimental yield for both RSM and ANN. The perfect straight line obtained indicated that the models factor and the predicted values are in agreement with each other. To check for the model accuracy, R^2, RSME and ADD of RSM and ANN were determined [10]. The results obtained indicated that the optimization tools certified are good

Table 5. Regression coefficients and significance of response surface quadratic.

Factor	CE	df	SE	95% CI low	95% CI high	VIF
Intercept	47.40	1	0.6345	45.90	48.90	-
X_1	0.6125	1	0.5016	−0.5737	1.80	1.0000
X_2	−1.60	1	0.5016	−2.79	−0.4138	1.0000
X_3	1.56	1	0.5016	0.3763	2.75	1.0000
X_1^2	−1.20	1	0.7094	−2.88	0.4776	1.0000
X_2^2	0.5250	1	0.7094	−1.15	2.20	1.0000
X_3^2	−3.10	1	0.7094	−4.78	−1.42	1.0000
X_1X_2	−0.7375	1	0.6915	−2.37	0.8976	1.01
X_1X_3	−0.3625	1	0.6915	−2.00	1.27	1.01
X_2X_3	−0.1375	1	0.6915	−1.77	1.50	1.01

Where: df = Degree of Freedom, CE = Coefficient of Estimation SE = Standard Error, CI = Confidence level, VIF = Variance Inflation Factor.
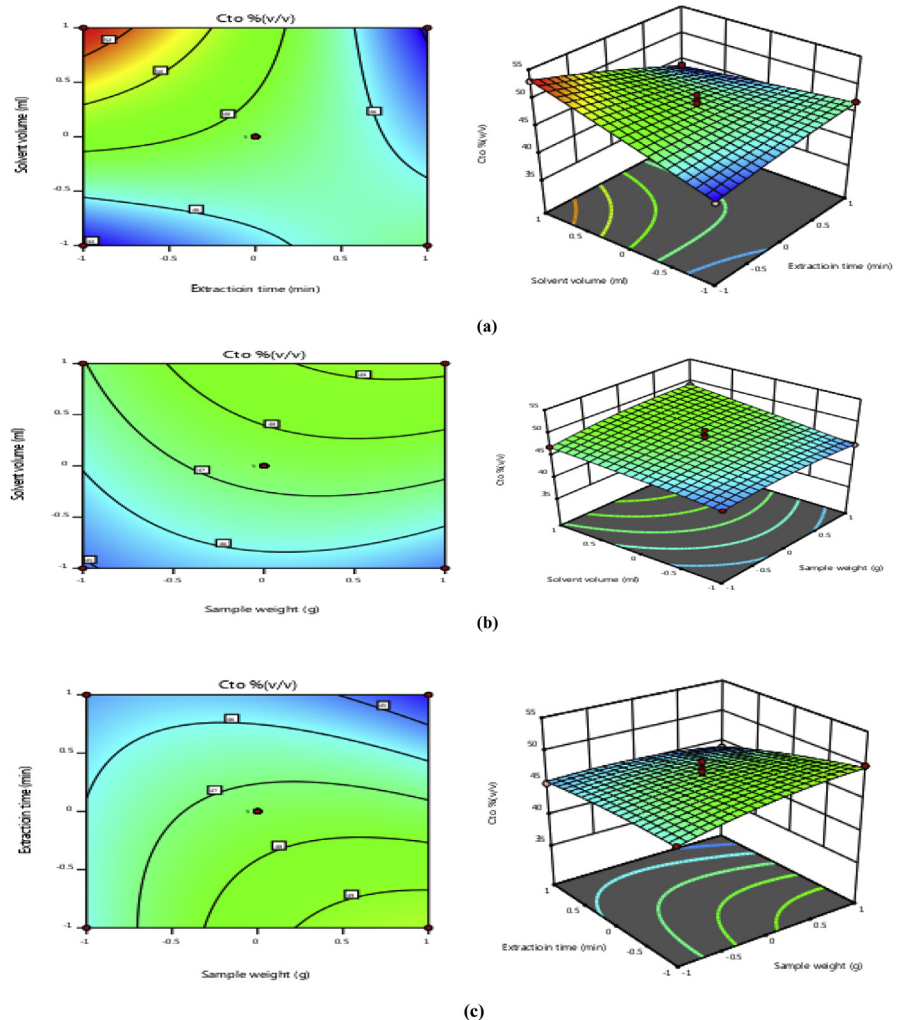
(a)

(b)

(c)

Fig. 3. The contour and 3D surface plots by RSM showing interactive effect of variables on Oil yield.

for predictions due to the high values of R^2 of 86.65% for RSM and 93.56% for ANN, respectively. Hence, it can be deduced that for the modeling and optimization of oil extraction from the oil seed, ANN showed a clear supremacy over RSM in terms of optimum oil yield and R^2 value.

3.2. Physicochemical properties of oil

Table 6 showed the result obtained while carrying out the physicochemical characteristics of the oil. It was noted that the oil was brownish yellowish liquid at room temperature, having a moisture content of 0.0011% with density of 0.9804 g cm^{-3}. Observation on the moisture content of the oil and the density showed a close agreement with what was earlier reported by [5]. The percentage FFA and acid values of the oil account for the good resistance of the oil to hydrolysis, the values of 2.3175 for FFA and 4.6350 for acid value showed that oil has high resistance to
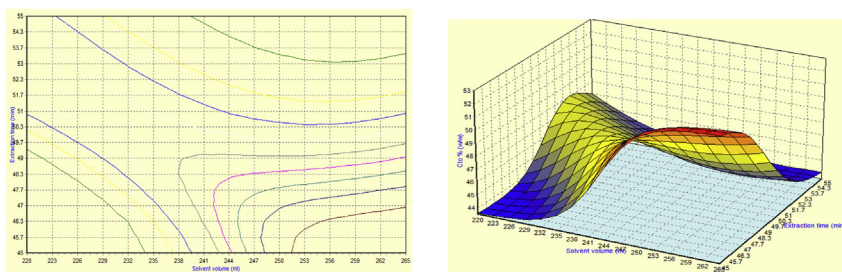
Plot of oil, reaction time and solvent volume
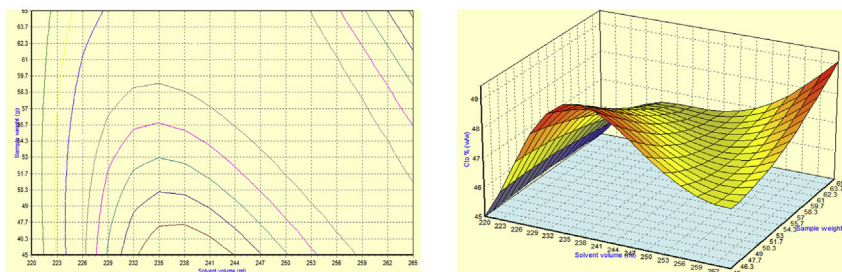
Plot of oil, sample weight and solvent volume
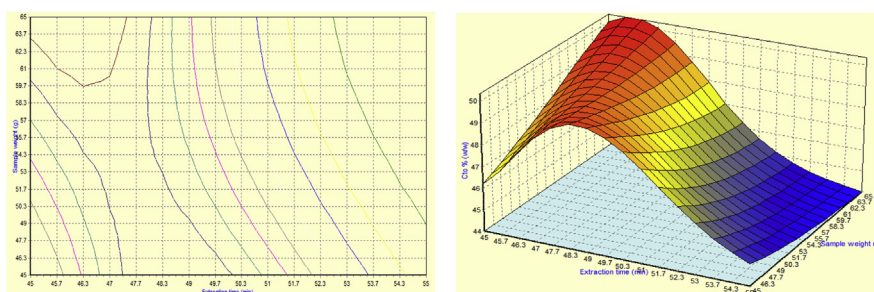
Plot of oil, reaction time and sample weight

Fig. 4. The contour and 3D surface plots by ANN showing interactive effect of variables on oil yield.

hydrolysis. The peroxide value, always account for the hydroperoxides in the oil [47], the low value of 33.6000 meq. O_2/kg obtained for oil in this study indicated a greater resistance to oxidation. High saponification value (75.25 mg KOH/g) and high iodine (87.60 gI_2/100 g) value indicated a minimum percentage of triglycerides of oil with substantial level of unsaturation. The higher heating value accounts for the latent heat of vaporization of water in the combustion products. The higher the value of HHV of the oil, the more suitable the oil is for use as biofuel. The value of 45.3588 MJ/kg obtained from this study shows the oil is a good raw material for biofuel production.

Fuel properties such as cetane number (CN), measures the fuel's ignition delay, combustion quality and account for biofuel standard with a minimum of 40 [48, 49]. The high value of 99.1216 computed reflects the presence of high fuel potential. The America petroleum institute value (API) and Diesel index of the oil were less than
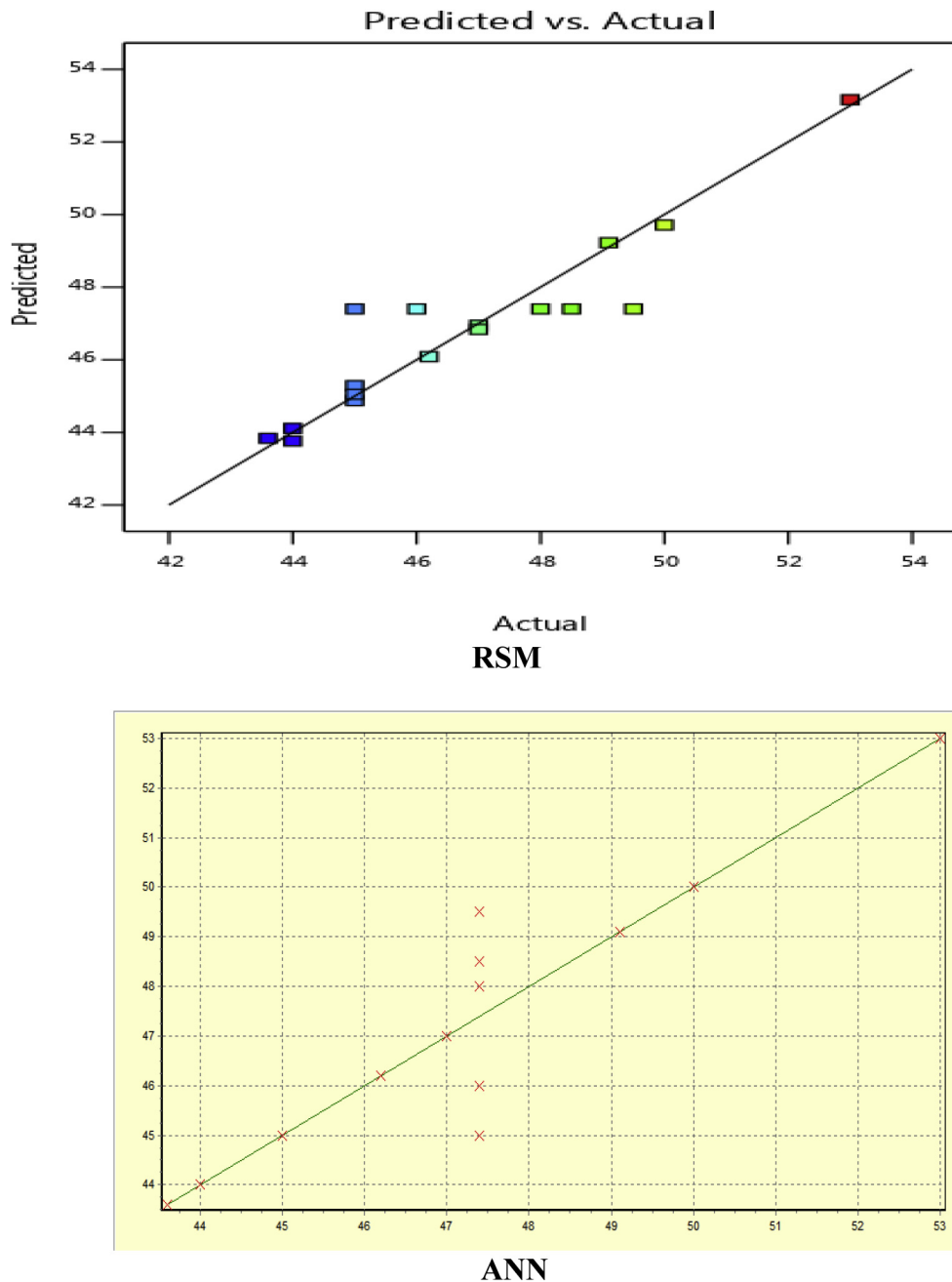
Predicted vs. Actual

RSM

ANN

Fig. 5. Linear correlation between experimental yields and predicted values for Oil.

that of AGO but are comparable with other values reported for most vegetable oil [50, 51].

3.3. Gas chromatographic analysis of oil

To identify the constituents of the volatile matter, long and branched chain hydrocarbons, alcoholic acids, esters and other components [52], GC-MS was employed. The

Table 6. Physicochemical of extracted *oil*.

Parameters	Cto
Physical properties	
Density (g cm^{-3})	0.9804
Physical state at 25 °C	Brownish yellowish in colour
Moisture content (%)	0.0011
Mean molecular mass	744.1860
Chemical properties	
%FFA (*oleic acid*)	2.3175
Acid value (mg KOH/g oil)	4.6350
Saponification value (mg KOH/g oil)	75.2500
Iodine value (g I$_2$/100 g oil)	87.6000
Peroxide value (meq O$_2$/kg oil)	33.6000
Higher heating value (MJ/kg)	45.3588
Other properties	
Cetane number	99.1216
API	12.8289
Diesel index	123.78
Aniline point (°F)	964.8566

results of the analysis led to the identification of the number of compounds from the GC fractions of oil. The oil is highly unsaturated with percentage unsaturation of 70.50% (Table 7).

3.4. EDXRF and SEM analysis of catalyst

Calcined four samples of pearl spar labelled A-D for 5 and 6 h were tested by using energy dispersive X-ray fluorescence (3600B) to determine the essential structures

**Table 7.** Percentage prevailing compound from gas chromatography analysis of oil.

S/N	Acids compounds	Percentage (%)
1	Linoleic	42.81
2	Oleic	28.69
3	Linolenic	10.52
4	Palmitic	8.76
5	Stearic	9.56
6	Other	0.35
	Total	**100**
	Unsaturation	70.50
	Saturation	29.50

Table 8. Results of calcinated samples analysis using EDXRF spectrophotometer.

Calcinated samples	A(pre-soaked)	B	C(pre-soaked)	D
Duration (h)	**5**	**5**	**6**	**6**
K contents	0.5848	0.5814	0.5789	0.5694

of the samples (Table 8). The patterns of calcined pearl spar with the relative abundance of the elements present are showed in Fig. 6. It was observed that the analysis of calcined catalyst resulted in detection of the elements present within the catalyst. Although, potassium dominates with the highest composition, follow by silicon and magnesium. Zirconium (Zr), Niobium (Ni) and Molybdenum (Mo) have closed value, while Tin (Tn) and Antimony (Sb) have the lowest values. The results obtained is in line with what was reported by [53], who demonstrated that potassium was found to have the highest conversion out of elements found in calcined banana peels used as catalyst in biofuel production via Napoleon's plum. Potassium (59.30%) was also found to be the highest element found in calcined cocoa pod husk used as catalyst in conversion of *Azadirachta indica* seed oil to biodiesel [54]. In this study, Calcined Pearl Spar earlier pre-soaked in methanol reached its highest concentration of 58.48% at a calcined time of 5 h for the peak value. This observation could be owing to spongy nature of the catalyst (see Fig. 7).

Results of the scanning electron microscope (SEM) of pearl spar samples showed a quantity of collections with tiny arrangement. The SEM images, engaged at the same resolution of 1 mm, showed the shiny, porousness and malleable nature of the atom
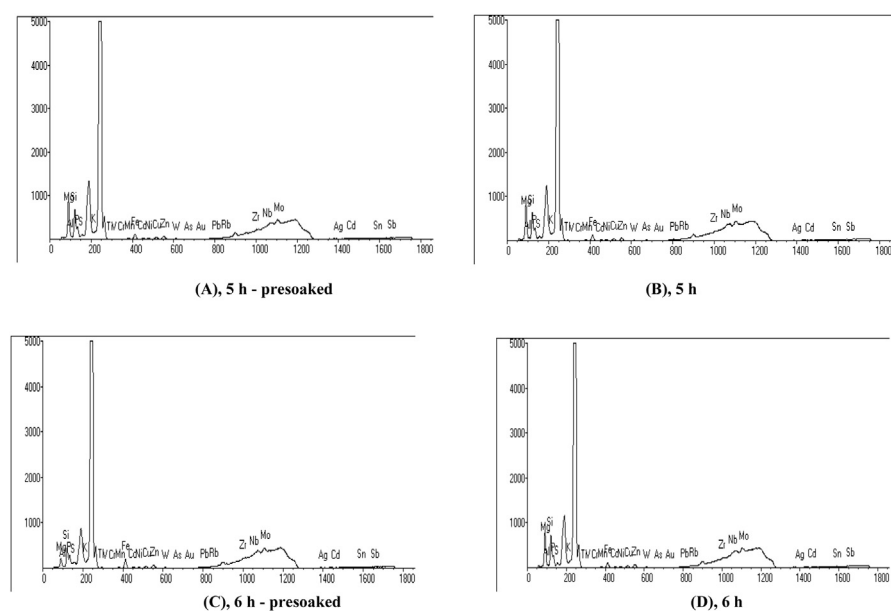
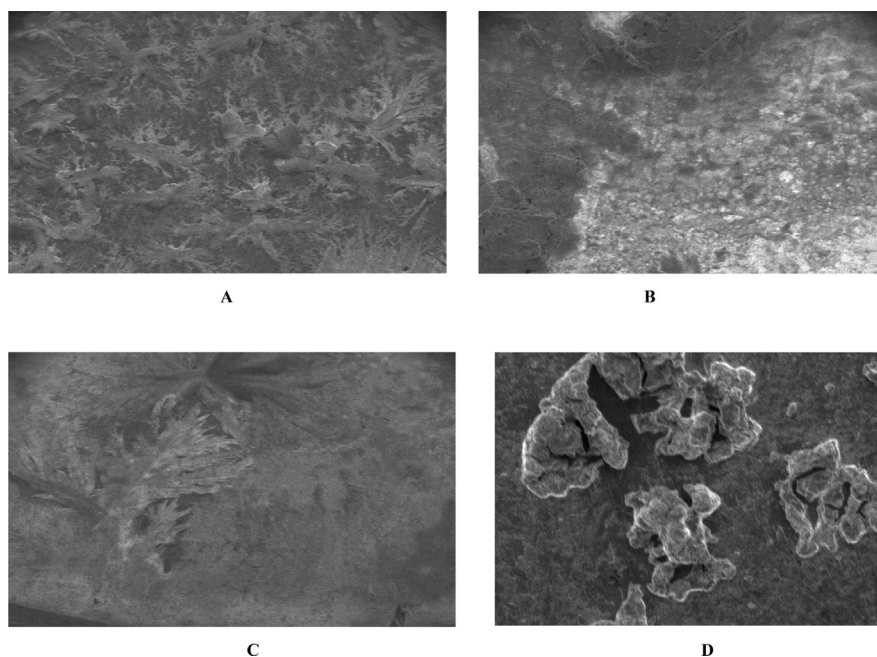**Fig. 6.** EDXRF pattern of pearl spar calcined @ 700 °C.

Fig. 7. Scanning electron microscopy (SEM) analysis for calcined pearl spar.

present. The actual calcination also ensued in the sintering of minor mineral collections and agglomerated atoms, which takes into action the malleable nature. It has been established that calcination always averts ooze of potassium, and may proliferate the reusability of catalyst [53].

3.5. Esterifying oil catalysed by acid

In an attempt to reduce the FFA of the oil, different acid/methanol volume ratios were used. The acid value and FFA was computed and recorded (Table 9). The optimum condition obtained for the pre-treatment of 100 ml of oil was established at a CH_3OH/acid volumetric ratio of 1.5 with an acid value of 1.2840 mg KOH g^{-1}, corresponds to FFA of 0.6142 mg KOH g^{-1} which was used for a successful conversion of oil to biodiesel [39, 53].

Table 9. Esterification condition with corresponding Acid and FFA values.

Methanol/acid volume ratio	Acid value (mg KOH g^{-1})	FFA (mg KOH g^{-1})
-	4.8048	2.9024
3.00	2.6920	1.3460
6.00	2.2792	1.1396
9.00	1.3536	0.6768
12.00	1.7896	0.8947
15.00	1.2840	0.6142
18.00	1.9820	0.9910

3.6. Transesterification of esterified oil by calcined pearl spar

Results in Table 10 showed the number of coded experimental runs, the results of the experiment carried out, the predicted values by both RSM and ANN and the residual values obtained. It was observed from the Table that the experimental highest bio-diesel obtained was 91.00% (w/w) at run 10 with coded values of $X_1 = 0$, $X_2 = +1$ and $X_3 = -1$. However, statistical analysis via RSM predicted 91.65% (w/w) at $X_1 = -0.999996$, $X_2 = -0.999996$ and $X_3 = -0.999996$, while ANN predicted 95.26% (w/w) at variable factors of $X_1 = -1.00$, $X_2 = -1.00$ and $X_3 = -1.00$, respectively.

Based on predicted values, the experiment was carried out in triplicates to validate the values predicted by RSM and ANN, and an average of biodiesel of 89.68% (w/w) and 92.87% (w/w) were obtained for RSM and ANN, respectively. Table 11 shows the results of the test of significance for every regression coefficient. It was observed that the p-values of X_1, X_2, X_3, X_2^2 and X_3^2 and X_1X_3 were the most significant model terms with $p < 0.05$. A higher F-value signifies a better fit of the RSM model to the experimental data [41]. According to [42], an F-value along with low p-value indicates a high significance of the regression model. Nevertheless,

Table 10. Coded experimental design results, biodiesel yield, predicted values by RSM and ANN and the residual values for the transesterification process.

Run	X_1	X_2	X_3	Biodiesel % (v/v)	Predicted		Residual	
					RSM	ANN	RSM	ANN
1	−1.000	−1.000	0.000	81	81.37	81.00	−0.3750	6.9066E-5
2	1.000	−1.000	0.000	75	74.63	75.001	0.3750	5.4253E-4
3	−1.000	1.000	0.000	83	83.38	83	−0.3750	2.1787E-5
4	1.000	1.000	0.000	76	75.62	76.00	0.3750	0.00033164
5	−1.000	0.000	−1.000	88	87.75	88.000	0.2500	5.9765E-5
6	1.000	0.000	−1.000	82	82.50	82.008	−0.5000	0.0081387
7	−1.000	0.000	1.000	81	80.50	81.175	0.5000	0.17461
8	1.000	0.000	1.000	71	71.25	71.00	−0.2500	4.0683E-4
9	0.000	−1.000	−1.000	89	88.88	88.955	0.1250	0.044601
10	0.000	1.000	−1.000	91	90.88	91.007	0.1250	0.076619
11	0.000	−1.000	1.000	80	80.13	80.153	−0.1250	0.15335
12	0.000	1.000	1.000	81	81.13	80.67	−0.1250	0.33007
13	0.000	0.000	0.000	73	73.20	73.201	−0.2000	0.20109
14	0.000	0.000	0.000	74	73.20	73.201	0.8000	0.79891
15	0.000	0.000	0.000	73	73.20	73.201	−0.2000	0.20109
16	0.000	0.000	0.000	73	73.20	73.201	−0.2000	0.20109
17	0.000	0.000	0.000	73	73.20	73.201	−0.2000	0.20109

Table 11. Test of significance for regression coefficient.

Source	SS	df	MS	F-value	P-value
X_1	105.12	1	105.12	358.96	<0.0001
X_2	4.50	1	4.50	15.37	0.0057
X_3	171.12	1	171.12	584.33	<0.0001
X_1^2	0.6737	1	0.6737	2.30	0.1731
X_2^2	111.67	1	111.67	381.32	<0.0001
X_3^2	200.46	1	200.46	684.51	<0.0001
X_1X_2	0.2500	1	0.2500	0.8537	0.3863
X_1X_3	4.00	1	4.00	13.66	0.0077
X_2X_3	0.2500	1	0.2500	0.8537	0.3863

the p-value should be lower than 0.05 for the model to be statistically significant [43]. Based on these reports, the regression model found in Table 12 was highly significant, as it was evident by the model F-value = 234.81 and the low p-values = 0.0001, respectively.

To test the fit of the model equation, the regression model was established using R^2 as a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions [44]. The R^2 value is always between 0 and 100% [37, 45]. However, to create a good-fit model, it was recommended that R^2 should not be less than 80% [46]. The results in Table 7 indicate an R^2 value of 99.69% which leaves only 0.31% of the variability not explains by biodiesel, this showed that unexplainable total variation could be due to other factors, which were not included in the model.

Shown in Table 13 is the result of analysis of variance of the regression equation model. The mathematical expression of the relationship between biodiesel and the variables factors is given in Eq. (15). All negative values have reduction impact on the biodiesel and positive values have ability to increase the yield.

Table 12. Analysis of variance (ANOVA) of regression equation.

Source	SS	df	MS	F-value	P-value
Model	618.89	9	68.77	234.81	<0.0001
Residual	2.05	7	0.2929		
Lack of fit	1.25	3	0.4167	2.08	0.2451
Pure error	0.8000	4	0.2000		
Cor. total	620.94	16			

RSM: R^2 = 99.67%, R^2 (adjusted) = 99.25%, R^2 (predicted) = 96.58%
ANN: R^2 = 99.94%, R^2 (adjusted) = 99.87%, R^2 (predicted) = 99.90%

Where: df = Degree of Freedom, MS = Means Square, SS = Sum of Square, F = Fischer, P = Probability.

Table 13. Regression coefficients and significance of response surface quadratic.

Factor	CE	df	SE	95% CI low	95% CI high	VIF
Intercept	73.20	1	0.2420	72.63	73.77	
X_1	-3.62	1	0.1913	-4.08	-3.17	1.0000
X_2	0.7500	1	0.1913	0.2976	1.20	1.0000
X_3	-4.63	1	0.1913	-5.08	-4.17	1.0000
$X_1{}^2$	0.4000	1	0.2637	-0.2236	1.02	1.01
$X_2{}^2$	5.15	1	0.2637	4.53	5.77	1.01
$X_3{}^2$	6.90	1	0.2637	6.28	7.52	1.01
X_1X_2	-0.2500	1	0.2706	-0.8898	0.3898	1.0000
X_1X_3	-1.00	1	0.2706	-1.64	-0.3602	1.0000
X_2X_3	-0.2500	1	0.2706	-0.8898	0.3898	1.0000

Where: df = Degree of Freedom, CE = Coefficient of Estimation SE = Standard Error, CI = Confidence level, VIF = Variance Inflation Factor.

$$Biodiesel/ctob \,\%(v/v) = +73.20 - 3.62X_1 + 0.75X_2 - 4.63X_3 + 0.4000X_1^2$$
$$+ 5.15X_2^2 + 6.90X_3^2 - 0.250X_1X_2 - 1.00X_1X_3$$
$$- 0.2500X_2X_3 \qquad (15)$$

The relationship between the variables and the response can be represented on graphical drawing, placing the experimental levels of each variable on the one side, and the type of interactions between the test variables, on the other, which allows deducing the optimum conditions. Figs. 8 and 9 therefore shows the contour and 3 dimensional surface plots for biodiesel under the viable optimum conditions for RSM and ANN. Meanwhile, the line graph helps to determine the relationship between two sets of values, with one data set always being dependent on the other set. Fig. 10 therefore shows a plot of the linear correlation between the biodiesel and the predicted value obtained from RSM and ANN. The perfect straight line obtained indicated that the models factor and the predicted values are in agreement with each other. Again, to check for the model accuracy, R^2, RSME and ADD of RSM and ANN were determined [10]. The results obtained showed that both optimization tools certified good predictions to be attained due to the value of R^2 of 99.67% for RSM and 99.94% for ANN, respectively. Hence, it can be said for the modeling and optimization of biodiesel from the Lucky nut oil, ANN showed a clear superiority over RSM in terms of optimum biodiesel yield and R^2 value.

3.6.1. Effects of Lucky nut seed on the properties of biofuel

Observation form the results showed that the Lucky nut seed is rich in oil, and its properties such as the density, low moisture content, higher heating value, the cetane number, the API and the diesel index proved it suitability for biofuel production. In addition, the high FFA and the high unsaturated acid value found in the Lucky nut
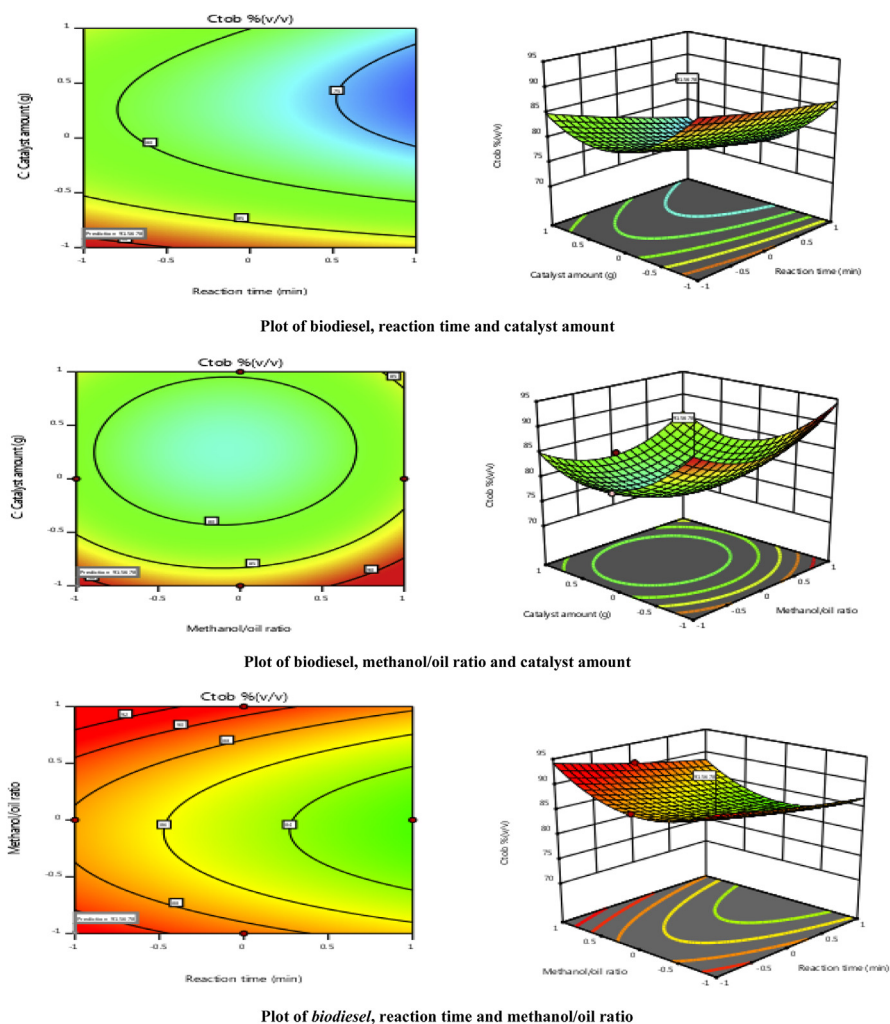
Plot of biodiesel, reaction time and catalyst amount

Plot of biodiesel, methanol/oil ratio and catalyst amount

Plot of *biodiesel*, reaction time and methanol/oil ratio

Fig. 8. The contour and 3D surface plots by RSM showing interactive effect of variables on biodiesel yield.

oil, showed its non-edibility. Hence, the Lucky nut proved its suitability for a good feedstock for environmental friendly biofuel.

3.6.2. Effects of the pearl spar on the properties of biofuel production

Elemental analysis results using EDXRF Spectrophotometer for calcined Pearl Spar revealed that the pre-soaked sample D was found with the highest potassium content (58.48%). The supplementary material showed the consistent spectrum with the comparative abundance of the elements present. Observation from this study implied that K is the major active component responsible for the activity of the catalyst in pearl spar synthesis which served as base catalyst for transesterification of esterified oil to biofuel. Reports showed that calcination always prevented leaching of
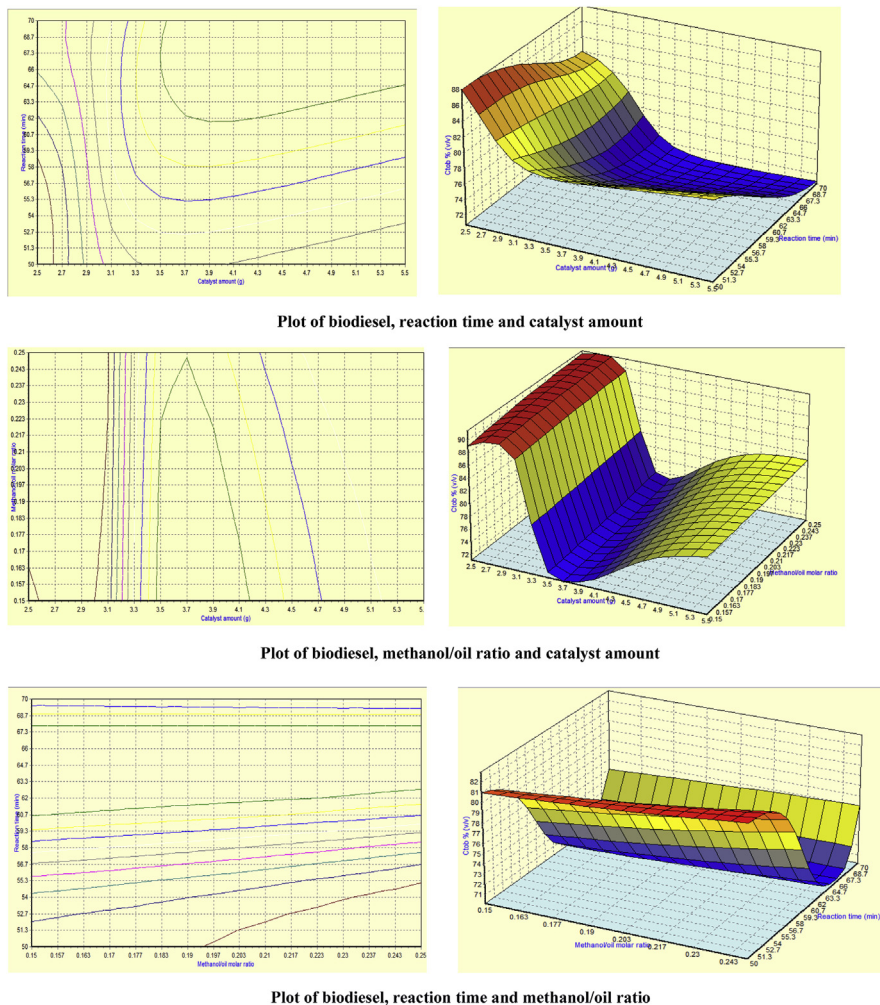
Plot of biodiesel, reaction time and catalyst amount

Plot of biodiesel, methanol/oil ratio and catalyst amount

Plot of biodiesel, reaction time and methanol/oil ratio

**Fig. 9.** The contour and 3D surface plots by ANN showing interactive effect of variables on biodiesel yield.

potassium, and may increase the reusability of catalyst during biofuel production [39]. These effects are always associated with higher heating values, high diesel index, high API and low aniline point.

3.7. Biodiesel properties as compared to other literature studies

The physicochemical analysis results of the biodiesel were compared with other published research works and also with ASTM D6751 and EN 14214 standards (Table 14). At room temperature, the biodiesel produced was brownish liquid having a low moisture content of 0.0010. Observation from [40, 54] showed that the produced biodiesel percentage moisture content is in line with what was reported. The density of 0.8720 g cm^{-3} was in reasonable agreement with other works and within the range specified by [40, 54]. The Lucky nut biodiesel acid value obtained
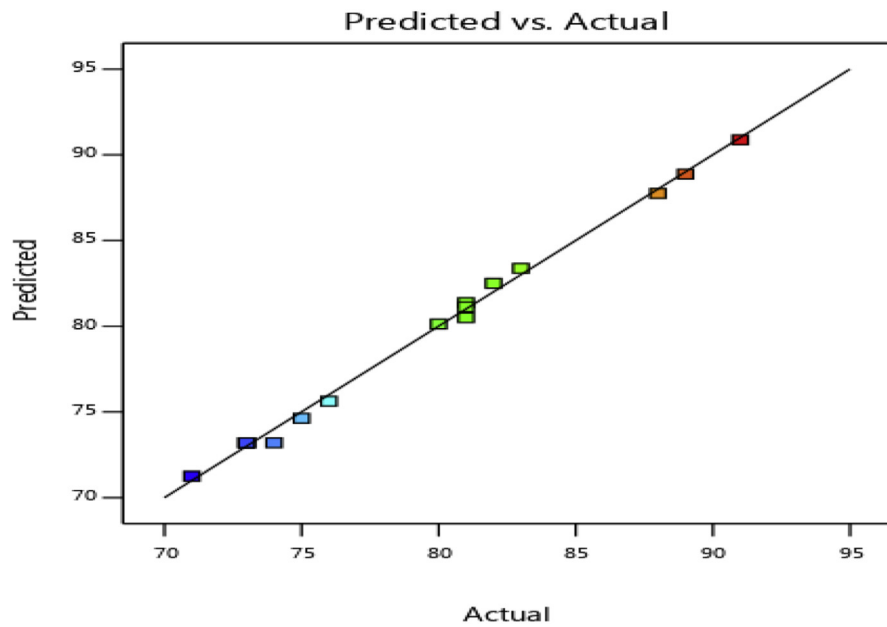
ANN
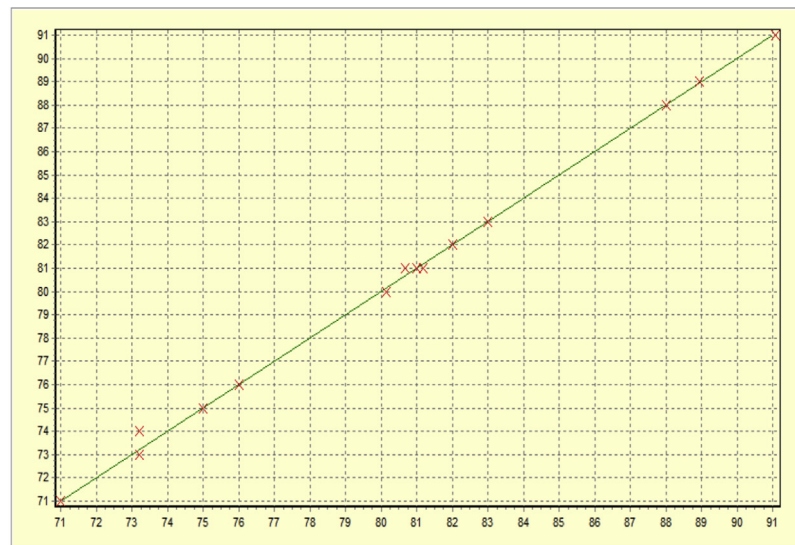
RSM

Fig. 10. Linear correlation between experimental yields and predicted values for biodiesel.

was 0.3200 mg of KOH/g oil, this value was higher than what was reported by [55, 56], but lower than the values reported by [4, 57] on the same feedstock. The iodine value of Lucky nut biodiesel of 80.4200 gI_2 /100 g oil obtained in this study was above the value recorded in [44, 55] but well below the prescribed maximum limit of [54]. The saponification value accounts for the number of milligrams of KOH,

Table 14. Qualities of biodiesel as compared with other researched work.

Properties	[55]	[57]	[56]	[4]	[40]	[54]	Ctob
Density (15 °C, g/cm^3)	0.875	0.86	0.87	0.887	0.84	0.86−0.90	**0.8720**
Acid value (mg KOH/g)	0.057	0.3	0.2	0.46	<0.80	0.5 max.	**0.3200**
Peroxide value (meq. O$_2$/kg oil)	-	-	-				**21.4300**
Iodine value (g I$_2$ /100 g)	69.9	-	-	-	-	120 max.	**80.4200**
Saponification value (mg KOH/g)	-	-	-	-	-	-	**76.4000**
Cetane number	61.5	-	54.2	123.25	47 min.	51 min.	**99.6228**
Moisture content (wt. %)	-	-	-	-	<0.03	0.02	**0.0010**
Cetane index	62.9	-	-	-	-	-	-
Mean molecular mass	-	-	-	-	-	-	**732.9840**
Higher heating value (MJ/kg)	-	-	-	-	-	-	**45.2512**
API	-	-	-	-	36.95	-	**30.7706**
Diesel index	-	-	-	-	50.4	-	**124.4710**
Aniline point (°F)	-	-	-	-	331	-	**404.5288**

required to neutralized the FFA resulting from the complete hydrolysis of 1 g of fat or oil, constituent of the oil. The value obtained in this work was 76.4000 mg KOH/g oil, but no value was recorded by other researchers in the previously published works. The HHV computed for Lucky nut biodiesel in this study was 45.2512 MJ/kg, which takes into account the latent heat of vaporization of water in the combustion products. Cetane number is a measure of the fuel's ignition delay and combustion quality of the oil/fuel. The higher the cetane number the shorter the delay interval and the greater the combustibility of the fuel. Fuels with a low cetane number are difficult to start the engine, hence producing smoke. The standard minimum specification value of the cetane number for biofuel is within the range of 47−51 [40, 54]. The values obtained by most authors were within the ranges of 47−61.5, but the value obtained from this work was higher (99.6228). The higher value obtained in this work may be attributed to the nature of the catalyst used during the transesterification process. Other properties, such as Aniline point, diesel index and API of the Lucky nut biodiesel were also found to be in the ranges earlier reported by most authors [50, 51].

3.8. Comparing the fuel properties of oil with biodiesel

Comparative analysis of the oil and biodiesel was carried out so as to determine the effects of catalytic conversion of oil to biodiesel. The results obtained are displayed in Table 15. From the table, it was observed that there was 9% reduction in biofuel moisture content when compared with the parent oil (*Lucky nut oil*). This decrease helps to prevent or eliminate an engine knockout effect. The density decreases by 11%, which showed a significant increase in heat of vaporization and accelerated

Table 15. Comparing the fuel properties of lucky nut oil and lucky nut biodiesel.

Parameters	*Cto*	*Ctob*
Density (g cm^{-3})	0.9804	0.8720
Moisture content (%)	0.0011	0.0010
Mean molecular mass	744.186	732.9840
Acid value (mg KOH/g oil)	4.6350	0.3200
Saponification value (mg KOH/g oil)	75.2500	76.4000
Iodine value (g I$_2$/100 g oil)	87.6000	80.4200
Peroxide value (meq. O$_2$/kg oil)	33.6000	21.4300
Higher heating value (MJ/kg)	45.3588	45.2512
Cetane number	99.1216	99.6228
API	12.8289	30.7706
Diesel index	123.7800	124.4761
Aniline point (°F)	964.8566	404.5288

ignition when combustion occurred. The iodine value was reduced by 8%, which implied that the biofuel produced contained low level of unsaturation [58], the acid value reduced by 95.5%, indicating the biodiesel has a long shelf life [59, 60]. The saponification value was increased by 1.5%, suggesting a high concentration of triglycerides in biodiesel. The higher heating value further decreased by 0.24%, Cetane number increased by 0.5%, which accounts for its greater combustion process ability, as a fuel with low cetane number produces smoke, when used in engine [61]. Other additional fuel properties, such as the diesel index and API increased from oil to biofuel. These results confirmed that the produced biodiesel could serve as an alternative to the conventional diesel and its blends could improve it fuel properties.

4. Conclusion

This study concluded that Lucky nut seed is very rich in oil with validated optimum yield of 46.82% (w/w) and 50.80% (w/w) by RSM and ANN, respectively, and the oil was highly unsaturated with a high FFA. Based on predicted values, the optimum validated biodiesel by RSM and ANN were 89.68% (w/w) and 92.87% (w/w), respectively. Calcined pearl spar earlier pre-soaked in methanol showed accurate ability to serve as a heterogeneous base catalyst for biofuel production from Lucky nut seed. The produced biodiesel has good properties and it is in line with reports published by other researchers using the same feedstock. Hence, the study concluded that the produced biodiesel could replace the conventional diesel with release of less hazardous emission.

Authors recommend that countries should invest in renewable energy sources by making use of non-edible oil over the use of fossil fuel and its derivatives for electricity generation.

Declarations

Author contribution statement

Tunde Adepoju: Performed the experiments; Wrote the paper.

Rasheed Babalola: Performed the experiments.

Olatunji Mathew: Design expert software analyst.

Ibeh Mayen: Contributed reagents, materials, analysis tools or data.

Ademiluyi Taiwo: Performed the experiments; Wrote the paper.

Babatunde Olatunbosun: Analyzed and interpreted the data.

Funding statement

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

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