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Biodiesel production from yellow oleander seed oil via heterogeneous catalyst: performance evaluation of minitab response surface methodology and artificial neural network

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Abstract

This study demonstrates biodiesel production from yellow oleander seed oil using RSM to optimize the process parameters. Process parameters such as catalyst amount, reaction time and methanol /oil ratio were considered in this study, physiochemical properties of the biodiesel produced were also determined. From the results, the optimal condition for biodiesel yield was established at catalyst amount of 10.34 (wt/wt)/%, reaction time of 70 minutes and methanol/oil ratio of 0.1 (v/v); theoretical biodiesel yield predicted under this condition by RSM and ANN was 86.13 % (v/v) and 86.19 % (v/v) respectively, this was validated as 86.00 % (v/v). The physicochemical characteristics of the biodiesel produced showed that the oil is a suitable feedstock for biodiesel production.

1. Introduction

In developing countries such as Nigeria, energy generation is considered as an important aspect of the economy. Due to increase in demand for energy, there has been a continuous research for different forms of energy that would meet up with the demand [1]. Many countries in the world are resorting to biofuel technology to solve the problem of the gradual increase in the rate of fuel and energy prices resulting from depletion in the world's non-renewable fossil fuels [1]. The world's major producers of biofuel are Brazil (ethanol), U.S.A (ethanol), Germany (biodiesel), and Austria (biodiesel). About 20 million drives up fuel tank in Brazil is cut with about 25 percent ethanol. In 2004 about $1.933x10^6$ tones of biodiesel were produced in Europe [2, 3].

Biodiesel has blossom as a greener and new renewable alternative to petroleum diesel, which is non-toxic, neutral, carbon, sulphur and aromatics free fuel [4, 5]. Biodiesel is an option to petro-diesel, which is obtained from vegetable oils in the presence of methanol and homogenous catalyst [6]. Biodiesel has similar physiochemical properties and engine performance as petroleum diesel fuel [7]. Biodiesel blend with conventional diesel up to 20% had served as fuels for diesel engines [8], which significantly reduces emissions [9, 10].

The application of heterogeneous or solid catalyst has continued to gain interest in biodiesel production. The catalysts are neither consumed nor dissolved in the reaction mixture which made it easier to be recovered from the product [11]. Besides that, the recovered catalyst can be reused back in the reaction, hence reducing the catalyst consumption and production cost [12]. The heterogeneous base catalyst offers several benefits including recoverability, less corrosive, easy separation and longer catalyst life [13 – 16]. It does not require additional separation costs when compared with homogeneous catalysts [17]. Several studies such as Deka and Basumatary, [18], Kakati et al. [19] have also examined the use of heterogeneous catalyst in the production of biodiesel.

Yellow oleander (Thevetia peruviana) tree is largely available in North-East India, and is widespread in American, Asian and African continents [20]. A yellow oleander tree can produce about 400–800 fruits all the year round depending on the climatic conditions and age of the plant, the fruits are usually green in colour and become black on ripening. Each fruit contains one to four seeds in its kernel; the oil content of the seed is about (60–65%) which makes it a naturally suitable source of renewable non-edible oil [20a]. Studies such as Adebowale et al. [21], Yarkasuwa et al. [22], Betiku and Ajala, [17] have examined its use for biodiesel production.

RSM has been used extensively in the optimization of seed oils to biodiesel; it was used by Betiku, and Adepoju, [23] in methanolysis optimization of sesame (*Sesamum indicum*) oil to biodiesel. Transesterification of *Moringa oleifera* oil to biodiesel was also optimized via RSM by Rashid et al. [24], Tiwari et al. [25] optimized biodiesel production from jatropha oil with high free fatty acids using RSM, Jeong et al. [26] optimized the transesterification process of animal fat ester, while Yuan et al. [27] used RSM for optimization of waste rapeseed oil with high FFA to biodiesel. Also, Zhang et al. [28] applied RSM for the optimization of Zanthoxylum bungeanum seed oil transesterification to biodiesel using CaO as catalyst. Optimization of transesterification variables for biodiesel production from cottonseed oil using RSM has also been reported by Rashid et al. [24].

ANNs is a artificial learning system that have been used in biotechnology [29], it has also been used in the field of medicine, metrology, neurology, biology, psychology, science, mathematics and engineering [30]. ANN has proved to be an efficient tool used in industrial research, especially when the several process variables are considered [31]. Artificial Neural Network has been used in determination of diesel engine performance and exhaust emission analysis using waste cooking biodiesel fuel by Ghobadiana et al. [32] whereas Ramadhas et al. [33] used it for the prediction of the cetane number of biodiesel. It was used for the optimization of operational conditions for biodiesel production from soybean oil and application of it for estimation of the biodiesel yield by Moradi et al. [34].

This present study considers optimization of biodiesel production from yellow oleander seeds; it considered catalyst amount, reaction time and methanol/oil ratio as process parameters. The physiochemical properties of the biodiesel produced were also determined in other to ascertain it's suitability as a feedstock for biodiesel production.

2. Material and Methods

2.1. Chemicals

Chemicals used were of analytical grade which include; n-Hexane, sodium hydroxide, potassium hydroxide, calcium chloride, methanol, ethanol, phenolphthalein, starch, sodium thiosulphate, ethanoic potassium hydroxide, hydrochloric acid, isooctane, diethyl ether, iso-octane and ethyl alcohol.

2.2. Yellow oleander seeds

Yellow oleander seeds used in this study were handpicked from secondary schools in Ile Ife, Osun state, Nigeria. Mesocarps and epicarp of the seeds were removed manually, and sundried for a week, after which it was shelled and decorticated. The kernels were sundried until constant weight was achieved. Separation of chaffs was carried out by winnowing; the seeds were milled into powder by grinding machine.

2.3. Soxhlet extraction

100 g of milled seeds were subjected to a total extraction time of 3 hours at 60^0C and 250 ml of n-hexane was used as solvent. The solvent present in the oil-solvent mixture was recovered and recycled by distillation.

2.4. Catalyst Activation

The limestone catalyst was manually grinded and prepared by pre-soaking in methanol and subjected to a high temperature of 700^0C in a (Carbolite AAF 11000) furnace for 5 hours according to Oyekunle [35]. EDXRF Spectrophotometer analysis was performed to examine the elemental analysis. Table 1 shows detailed chemical compositions of the catalyst which indicate high calcium (Ca) content of 57.33% which was useful for transesterification process.

Table 1: EDXRF Spectrophotometer analysis

Element	Ca	Mg	Si	Sn	Sb	Al	Fe	S	P	Mo	W	Au	Zn
Wt.%	57.33	12.02	1.41	0.61	0.53	0.53	0.40	0.30	0.25	0.20	0.08	0.08	0.07

2.5. Biodiesel production process

The catalyst amount ranged from 2 to 6g was dispersed in methanol at a temperature of 60^0C for a period of time prior to contact with the preheated feedstock (50 ml of oil) placed on a hot plate magnetic stirrer, providing a robust transesterification catalyst system. Transesterification process was performed at various reaction time, at the end of the experiment, the product was gently poured into a separating funnel where two phases separate; less dense biodiesel at the upper layer while residual catalyst and glycerol at the lower layer. Residual catalyst, methanol and glycerol were removed by washing intensely with warm water. The washed biodiesel produced was dried over heated calcium chloride powder (1g) placed on a hot plate to absorb untapped water. The dried biodiesel obtained was decanted into a clean pyrex flask to remove the hygroscopic calcium chloride sediment at the bottom of the heated flask. Biodiesel yield was determined on weight basis.

2.6. Analysis of biodiesel produced

The physiochemical analysis of biodiesel produced was carried out according to ASTM D6751 methods which were being used to obtain, acid value (ASTM D664), moisture content (ASTM D2709), density (ASTM D5002), free fatty acid (FFA) (ASTM D5555), saponification value (ASTM D464), specific gravity (ASTM D287) and cetane number (ASTM D613). Peroxide value was determined based on American Oil Chemists' Society [28]. Iodine value was estimated by applying Wijs method [37, 38].

2.7. Experimental Analysis of biodiesel produced and RSM stastistical Analysis.

In this study, the independent variables considered for the optimization process include catalyst amount (X_1), reaction time (X_2) and methanol/oil ratio (X_3). The coded and uncoded levels of the independent variables are shown in Table 2 while the RSM for the transesterification process generated by Box-Behnken design Minitab 15.5 statistical software is displayed in Table 3. The experimental data obtained were analysed by the response surface regression procedure using second-order polynomial (Eq. 1)

$$R_F = \mu_0 + \mu_1 X_1 + \mu_2 X_2 + \mu_3 X_3 + \mu_{1,1} X_1^2 + \mu_{2,2} X_2^2 + \mu_{3,3} X_3^2 + \mu_{1,2} X_1 X_2 + \mu_{1,3} X_1 X_3 + \mu_{2,3} X_2 X_3 \quad (1)$$

Where R_F is the predicted response (biodiesel yield), μ_0 is the intercept term, μ_1, μ_2, μ_3 are linear coefficients $\mu_{1,2}$ $\mu_{1,3}$, and $\mu_{2,3}$ are the interactive coefficients $\mu_{1,1}$, $\mu_{2,2}$, and $\mu_{3,3}$ are quadratic coefficients.

Table 2: Experimental range and levels of independent variables.

Variable	**Symbol**	**Coded factor levels**		
		-1	**0**	**+1**
Catalyst amount(wt/wt)%	X_1	5.17	10.34	15.50
Reaction time(min)	X_2	50.00	60.00	70.00
Methanol/oil ratio(v/v)	X_3	0.10	0.15	0.20

2.6. ANN Data Verification

The predicted responses obtained from ANN were compared with experimental responses in order to determine the efficacy of the optimization tool. The coefficient of determination (R^2) which is a measure of the amount of reduction in the variability of the response by using the repressor variables [39] was determined to identify the best models by comparing the evaluated values for the models. The R^2 was calculated according to Betiku and Ajala [17] as shown in Eq. 2

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

Where n is the number of experimental data, $x_{i,cal}$ is the calculated values, $x_{i,exp}$ is the experimental values and $x_{avg,exp}$ is the average experimental values.

Table 3: Box-Behnken Design of Transesterification Process by RSM and ANN

Run	X_1	X_2	X_3	Biodiesel yield (v/v)	Predicted		Residual	
					RSM	ANN	RSM	ANN
1	1	0	1	56.00	56.25	55.93	-0.25	0.07
2	1	-1	0	60.00	59.88	60.63	0.13	0/63
3	0	1	-1	86.00	86.13	86.19	-0.12	0.19
4	-1	1	0	78.00	78.13	78.02	-0.12	0.02
5	0	0	0	58.00	58.00	58.02	0.00	0.02
6	0	1	1	76.00	75.88	75.98	0.13	0.02
7	-1	-1	0	77.00	77.13	76.99	-0.12	0.02
8	0	0	0	58.00	58.00	58.02	0.00	0.02
9	1	0	-1	66.00	66.00	66.08	0.00	0.08
10	0	0	0	58.00	58.00	58.02	0.00	0.02
11	-1	0	-1	83.00	82.75	82.99	0.25	0.01
12	0	-1	1	75.00	74.88	75.02	0.13	0.02
13	1	1	0	62.00	61.88	61.34	0.13	0.66
14	-1	0	1	73.00	73.00	73.00	0.00	0.00
15	0	-1	-1	84.00	84.13	83.81	-0.12	0.19

3. Results and discussion

3.1. Oil extraction

Essential oils was extracted from yellow oleander seeds. The average oil yield was found to be about 44.00 wt%, this was done in different batches, in other to get sufficient amount of oil that was required for the biodiesel production process.

3.2. Optimization of biodiesel production parameters by RSM

Results of biodiesel production using Box-Behnken design by Minitab 15.5 are presented in Table 3. Table3 illustrate coded factors considered in this work with experimental results, predicted and residual values obtained from RSM. The regression equation that described the biodiesel production process is presented in Eqn. 3

$$R_F\ (v/v\,\%) = 581.63 - 5.438X_1 - 13.100X_2 - 1417.5X_3 + 0.0625X_1^2 + 0.11000X_2^2 + 4500.0X_3^2 + 0.01250X_1X_2 - 0.500X_2X_3 \quad (3)$$

Table 4 illustrate test of significance for every regression coefficient and ANOVA results. The results showed the three linear terms (X_1, X_2, X_3,), and two quadratic terms (X_2^2, X_3^2) were all remarkably significant model terms at 95% confidence level except at X_1^2, X_1X_2, X_2X_3 based on the p-value of the terms i.e $p < 0.05$. However, based on the large F values and low corresponding p values, all the linear terms (X_1, X_2, and X_3) had high effects on the biodiesel yield. The model F value of 4835.25 with a low probability value ($p < 0.0001$) implied a high significance for the regression model according to Yuan et al. [27].

The goodness of fit of the model was checked by the coefficient of determination (R^2), which should be at least 0.80 for the good fit of a model [23, 40]. The R^2 value of 99.98% indicated that the sample variation of 99.98% of biodiesel was attributed to the independent variables, and only 0.03% of the variations were not explained by the model. The value of the adjusted R^2 (99.96%) was also very high, supporting a high significance of the model [41, 42], the Predicted R^2 of 99.84% is in reasonable agreement with the Adjusted R^2 of 99.96% which indicated the efficacy of the model for the adequate representation of the relationship among the selected variables.

Table 4: Test of significance for every regression coefficient and ANOVA results.

Source	DF	Seq SS	Contribution%	Adj SS	Adj MS	F-value	p-value
X_1	1	561.13	34.81	561.13	561.13	13467.00	0.00
X_2	1	4.50	0.28	4.50	4.50	108.00	0.00
X_3	1	190.13	11.79	190.13	190.13	4563.00	0.00
X_1^2	1	6.70	0.42	0.23	0.23	5.54	0.06
X_2^2	1	381.50	23.67	446.77	446.77	10722.46	0.00
X_3^2	1	467.31	28.99	467.31	467.31	11215.38	0.00
X_1X_2	1	0.25	0.02	0.25	0.25	6.00	0.05
X_2X_3	1	0.25	0.02	0.25	0.25	6.00	0.05
ANOVA							
Model	8	1611.75	99.98	1611.75	201.47	4835.25	0.00
Lack-of-Fit	4	0.25	0.02	0.25	0.06	*	*
Pure Error	2	0.00	0.00	0.00	0.00		
Total	14	1612.00	100.00				
R^2 = 99.98% R^2 (adjusted) = 99.96% R^2 (predicted) = 99.84%							

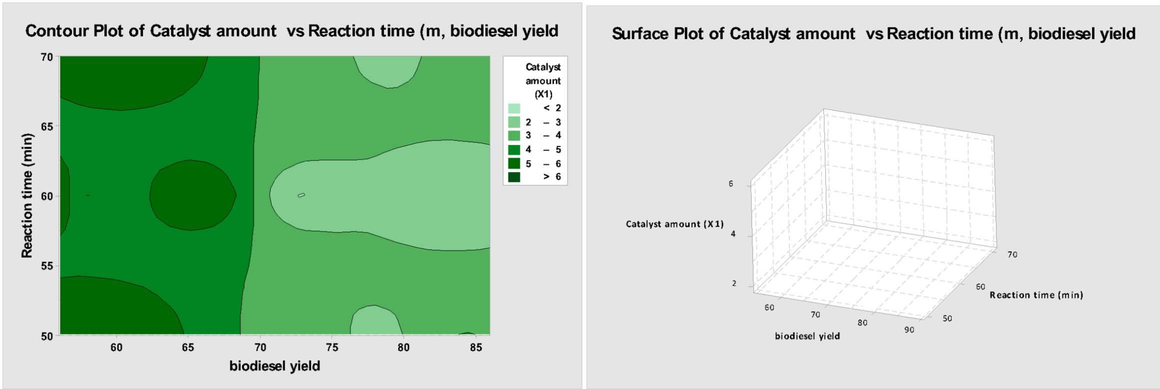
DF = Degree of Freedom, Seq SS = Sequential Sum of Square, Adj SS = Adjusted Sum of Square, Adj MS = Adjusted Mean Square, F = Fischer, p = Probability.

The significance of each coefficient in the experimental model was also determined by T-value and p – value (Table 5). A high T-test value with a low probability value indicated a high significance [43, 44]. Student's T test of each coefficient of the model showed that linear coefficient (X_2), all quadratic term (X_1^2, X_2^2, X_3^2) and cross product (X_1X_2) have significant effects ($P > |T| < 0.05$) on the biodiesel yield. All other terms (X_1, X_3, X_2X_3) displayed on Table 5 are not significant. The low values of standard error observed in the intercept and all the model terms demonstrated that the regression model was adequate, and the prediction was good [23]. The variance inflation factor (VIF) obtained in this study showed that the centre points are orthogonal to all other factors in the model.

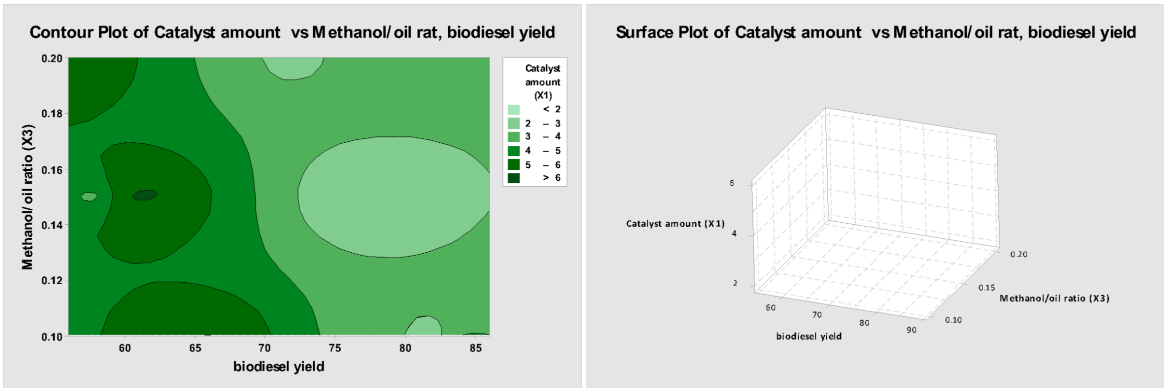
Table 5: ANOVA for response surface quadratic model for intercept

Term	Coefficient	Standard Error Coefficient	95% CI Low	95% CI High	T-Value	P-Value	VIF
Constant	58.00	0.1180	57.712	58.288	492.15	0.000	
X_1	-8.375	0.0722	-8.5516	-8.1984	-116.05	0.000	1.00
X_2	0.75	0.0722	0.5734	0.9266	10.39	0.000	1.00
X_3	-4.875	0.0722	-5.0516	-4.6984	-67.55	0.000	1.00
X_1^2	0.25	0.1060	-0.01	0.51	2.35	0.057	1.01
X_2^2	11.00	0.1060	10.74	11.26	103.55	0.000	1.01
X_3^2	11.25	0.1060	10.99	11.51	105.9	0.000	1.01
$X_1 X_2$	0.25	0.1020	0.00	0.50	2.45	0.050	1.00
$X_2 X_3$	-0.25	0.1020	-0.50	0.00	-2.45	0.050	1.00

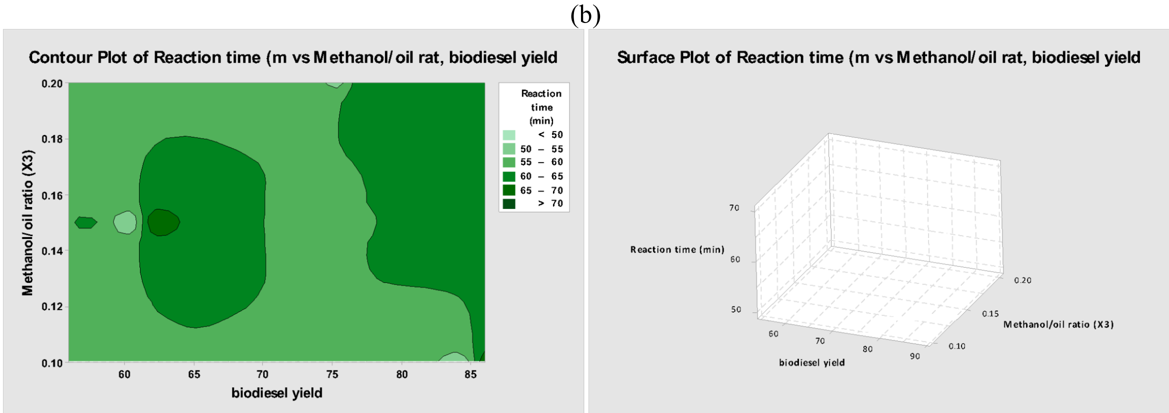
Two dimensional and three dimensional response plots are presented in Figure 1, this plots illustrate the interactions among the process parameters. The interactive effect of catalyst amount and reaction time on biodiesel yield is presented in Figure 1a. At lower catalyst amount there was increase in biodiesel yield, while increase in extraction time does not significantly affect biodiesel yield (Figure 1a). Figure 1b show the effect of catalyst amount and methanol/oil ratio on biodiesel yield, there was a high yield of biodiesel at the lowest catalyst amount and high methanol/oil ratio however, there was significant increase in biodiesel yield at lower methanol/oil ratio. Although Figure 1c shows a high yield of biodiesel at low reaction time and methanol/oil ratio when compared with their respective highest value, but maintaining a high reaction time with the lowest methanol/oil ratio gave the optimum yield, this goes on to prove that reaction time has little significance on biodiesel yield.



(a)



(b)



(c)

Figure 1: The Contour and Surface Plots showing interactive effect the variables on biodiesel yield

3.3. Optimization of biodiesel production parameters by ANN.

Table 3 shows the predicted and residual results by ANN with their corresponding experimental results. The optimum yield as predicted by ANN was 86.13% while the experimental biodiesel yield was 86.00%. This was clearly illustrated by the curvatures' nature as plotted by ANN of three dimensional surfaces in Figure 2, which shows the effect of catalyst amount with reaction time (Figure 2a), catalyst amount with methanol/oil ratio (Figure 2b), and reaction time with methanol/oil ratio (Figure 2c) on biodiesel yield. The importance level of the variables considered for biodiesel production in this study clearly shows that catalyst amount was the most important with 53.54%, followed by methanol/oil ratio of 41.31% and finally, reaction time of 5.15% (Figure 3).

3.4. Comparison of RSM and ANN Models

For both models (RSM and ANN) the optimal condition for biodiesel yield (86.00%) was established at catalyst amount of 10.34 (wt/wt)%, reaction time of 70 minutes and methanol/oil ratio of 0.1 (v/v). The theoretical biodiesel yield predicted under this condition by RSM and ANN was 86.13% and 86.19% respectively, the predicted value of ANN was higher when compared with RSM although, at the lowest biodiesel yield (56.00%) the predicted value of ANN (55.93%) was lower than RSM (56.25%). The equivalence plot by ANN and RSM shows a satisfactory correlation between the experimental and predicted values of the biodiesel produced (Figure 4).

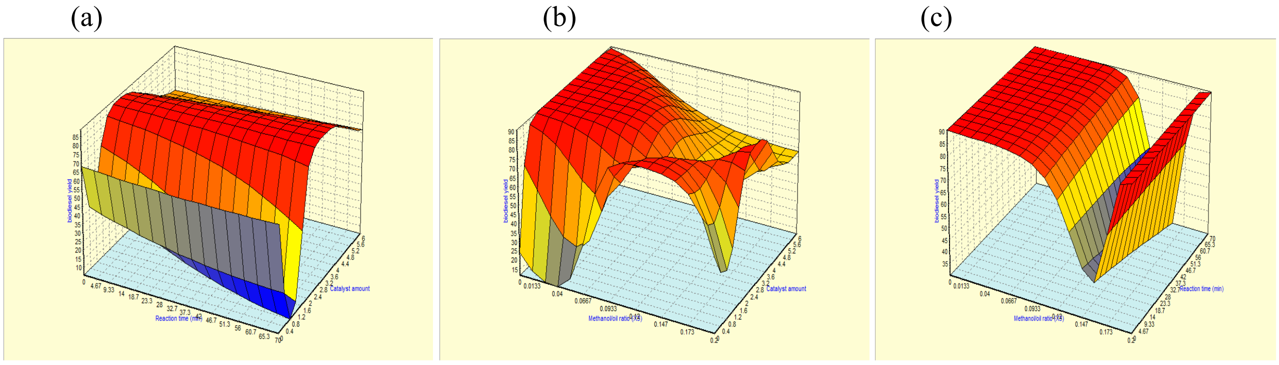


Figure 2: Three dimensional plot showing effect of (a) catalyst amount with reaction time (b) catalyst amount with methanol/oil ratio and (c) reaction time with methanol/oil ratio.

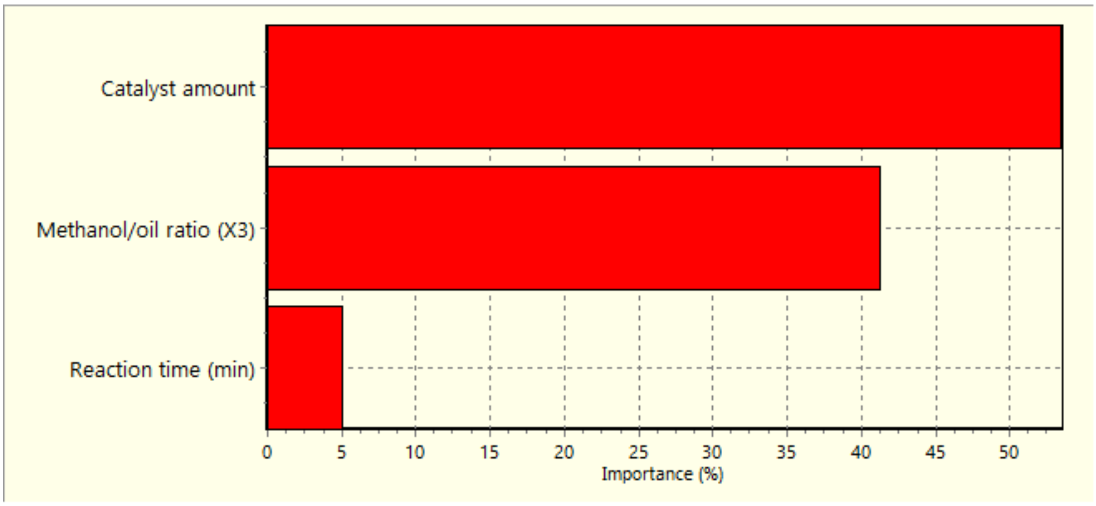


Figure 3: Importance of effective parameters on percentage biodiesel production.

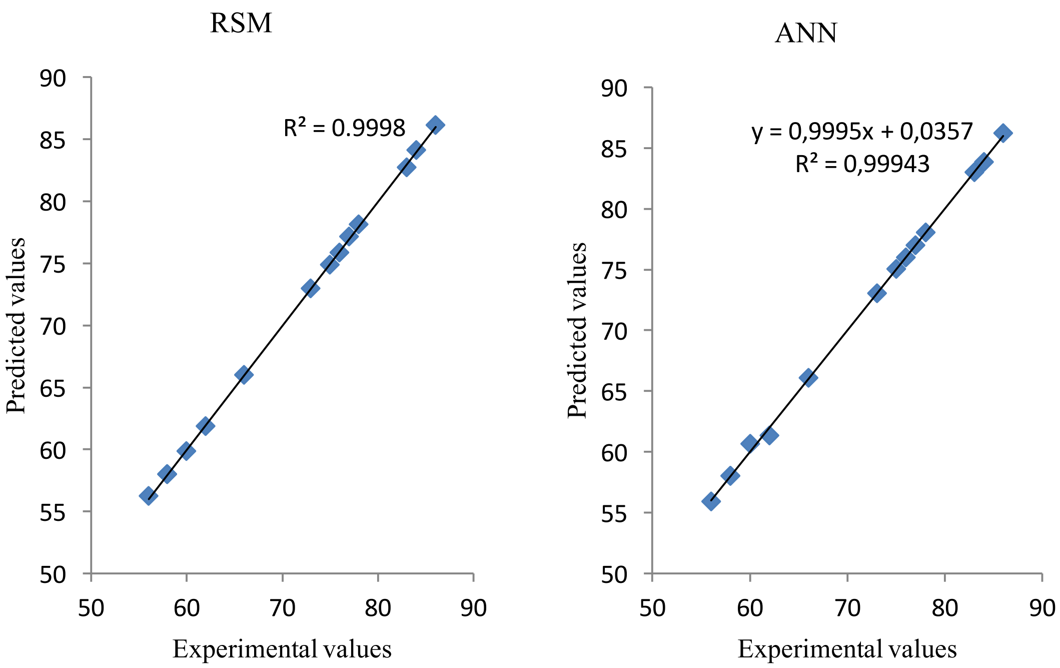


Figure 4: Equivalence plot for predicted against experimental values

In order to determine the accuracy of both models (RSM and ANN), the value of R^2 was evaluated. The result depicts that both optimization tools gave good predictions due to the high value of R^2 (99.98% and 99.94% for RSM and ANN respectively). However, for this study RSM showed a clear superiority over ANN because of the higher value of R^2.

3.5. Quality characterization of the biodiesel

The quality of biodiesel produced was evaluated by determining its physicochemical properties and the results were compared with previous studies as presented in Table 6. Biodiesel produced was reddish-brown in colour at room temperature with moisture content of 0.0044%, this was within ASTM D6751 standards of 0.03 and EN14214 standard of 0.02, low moisture content is required to prevent engine knockout effect which makes the biodiesel produced in this study suitable for use. Specific gravity observed in this study was lower than ASTM D6751 standards of 0.86-0.90 and EN 14214 standards of 0.85; specific gravity of the biodiesel in this study should be further improved upon so as to form a stable blend of biodiesel and petrodiesel. From Table 6, the density of the biodiesel produced was found to be slightly lower than studies by Balusamy et al. [45], Deka et al. [18], Adebowale et al. [21], and Betiku and Ajala [17] this was also lower than ASTM D6731 standards of 0.84 but within the range specified by EN 14214 of 0.86-0.90. The acid value of biodiesel produced was found to be 0.5076 mg of KOH/g which was within ASTM D6751 standards (< 0.80) and slightly higher than EN 14214 standards of biodiesel of 0.50 mg of KOH/g, this indicates the biodiesel produced has a long shell life [46]. Iodine value of biodiesel produced (73.2 g I_2 /100 g) was far below the maximum limit of 120 prescribed in EN 14214, which makes it suitable for use. The saponification value of the biodiesel produced was found to be 26.648, this gives an indication of the nature of the fatty acids present and thus, depends on the average molecular weight of the fatty acids present, it also represents the number of milligrams of KOH required to neutralize the fatty acids resulting from the complete hydrolysis of 1g of fat or oil.

In this study, the cetane number was higher than previous studies by Balusamy et al. [45], Deka et al. [18], Adebowale et al. [21], and Betiku and Ajala [17], which may be due to the high oxygen content present in the oil. The higher the cetane number the shorter the delay interval and the greater the combustibility. Fuels with low cetane number are difficult to start, hence it smokes. Standard minimum specification value of cetane number for biodiesel is within the range of 47-51 (ASTM D6751 and EN 14214). Cetane number obtained in this study (234.58) showed that it is of a very high fuel potential. Diesel index obtained in this study was higher than study by Betiku and Ajala [17] but lower than ASTM D6751 standard of 331 while the API obtained was lower than study by Betiku and Ajala [17] and ASTM D6751 standard of 36.95. These results showed that further improvements on the fuel properties (such as the specific gravity, acid value, diesel index and API of the biodiesel produced) could adequately enhance its use as an alternative to conventional diesel.

Table 6: Comparison of Physiochemical properties biodiesel produced with previous studies.

Properties	**Balusamy *et al.* [45]**	**Deka *et al.* [18]**	**Adebowale *et al.* [21]**	**Betiku and Ajala [17]**	**This study**
Density (15 ºC, g/cm^3)	0.839	0.875	0.870	0.887	0.816
Acid value (mg KOH/g)	-	0.057	0.200	0.460	0.508
Free fatty acid (%)	-	-	-	-	0.254
Iodine value (g I_2 /100 g)	-	69.900	-	90.230	73.200
Saponification value (mg KOH/g)	-	-	-	-	26.648
Cetane number	47.000	61.500	54.200	123.250	234.58
Moisture content (wt.%)	-	-	-	-	0.0044
Specific gravity (g/cm^3)	-	-	-	-	0.9130
API	-	-	-	28.030	23.484
Diesel index	-	-	-	157.290	311.918

Conclusion

The experimental results reported in this paper revealed that calcinated limestone is a potential catalyst for biodiesel production. The optimal reaction conditions of variables established for biodiesel production are catalyst amount of 10.34 (wt/wt)%, reaction time of 70 minutes and methanol/oil ratio of 0.1 (v/v). Using these optimal factor values under experimental conditions in three independent replicates, an average content of 86.00% (v/v) was achieved. Although both models gave a good R^2 value but RSM gave a higher R^2 value of 99.98% when compared with ANN (R^2 value of 99.94%). The physiochemical properties of the biodiesel revealed that oleader seed oil is a suitable feedstock for biodiesel production.

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