

Production of Biodiesel Using Calcium Oxide (CaO) Nanoparticle Synthesized from Chicken Eggshell

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Abstract - Application of low cost high free fatty acids (FFA) feedstock may reduce its overall cost of production. Transesterification reaction process was performed to produce biodiesel using crude palm oil, and the process provided higher biodiesel yield of 80% but somehow low in comparison to EN 14214 (96.60 %). The oil was transesterified using an alcohol (methanol). All the experimental runs carried out were designed using central composite design (CCD) coupled with surface response methodology (RSM) software (Design-Expert 12 software – the latest version (Stat-Ease Inc., USA). Thus, the yield obtained varies from 58% to 80%, the lowest yield was found to be 58% while the highest yield for this production was found to be 80%. With these results, it is clear that CaO nanoparticle is a good catalyst for catalysis in production of biodiesel.

Keywords - Biodiesel, Calcium Oxide (CaO), Nanoparticle Synthesized, Chicken Eggshell.

I. INTRODUCTION

Petroleum-based fuels are limited reserves concentrated in certain regions of the world. These sources are in the verge of getting extinct. The scarcity of known petroleum reserves will make renewable energy resources more attractive. Biodiesel obtained from energy crops produces favorable effects on the environment, such as a decrease in acid rain and in the greenhouse effect caused by combustion. Due to these factors and to its biodegradability, the production of biodiesel is considered an advantage to that of fossil fuels. In addition to this, it also shows a decrease in the emission of CO₂, SO₂ and unburned hydrocarbons during the combustion process [11].

In Nigeria, biodiesel (liquid biofuel from vegetable oils or animal fats) seems to be of the promising alternative to fossil fuels. This is because the crops required for biodiesel production are cultivated in large quantity, under favorable climatic conditions. The global biodiesel production has grown from approximately 5 million gallons in 2001 to 250

million gallons in 2006. Although high oil prices have lately tended to reduce production of biodiesel, several forces may contribute to long-term expansion in the biodiesel industry. High petroleum prices are raising diesel prices and the likely increasing costs of future oil production; Depletable resources follow Hotelling's prices in the long run and tend to increase over time, as petroleum is depleted; Government mandates, such as the provisions of the Energy Independence and Security Act of 2007 that includes mandates of up to 36 million gallons of biofuels; the public and government's concern over global warming may provide a value for biodiesels carbon-dioxide (CO₂) recycling characteristics [9].

A. Feedstock

Feedstock contributes a major share in the cost of the production of biodiesel fuel. The selection of feedstock is depended chiefly on its cost and availability. Countries such as United States of America and those belonging to European community are self-dependent in the production

of edible oils and even have surplus amount to export. Hence, edible oils such as rapeseed and soybean are used in European Nations and United States of America, respectively. Similarly, countries with coastal area such as Malaysia and Indonesia have surplus palm oil and are utilized for the production of biodiesel. In general, feedstock for the production of biodiesel can be classified into three groups: animal fats, vegetable oils (edible or non-edible oils), and used waste cooking oil. If we consider the top ten countries in terms of absolute biodiesel synthesis, the average feedstock dependence is 20% for animal fats, 11% for coconut oil, 22% for palm oil, 28% for soybean oil, and 5% each for rapeseed, sunflower and olive oils [12].

B. Vegetable Oil

This is a flammable or non-flammable, viscous, greasy, liquid substance at room temperature and insoluble in water but soluble in organic compounds which is derived from plants, animals or minerals deposits or manufactured artificially and can be used for food, as fuel, and lubricant. There are quite a lot of seeds and nuts which are rich in terms of oil contents, thus Soya beans, groundnut and palm kernel, pipe or mustard seed sesames, all are important sources of edible oils [12].

C. Advantages

Advantages of biodiesel as diesel fuel are liquid nature portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content,

higher cetane number (CN) and higher biodegradability. Main advantages of biodiesel given in the literature include domestic origin, reducing the dependency on imported petroleum, biodegradability, high flash point and inherent lubricity in the neat for [12].

D. Production techniques

There are four primary options for production biodiesel from fats and oils which include; direct/blends, microemulsion, pyrolysis and transesterification [23], [23].

E. Acid-catalytic transesterification methods

Biodiesel produced by transesterification reaction can be catalyzed by sulfuric, phosphoric, hydrochloric and organic sulfonic acids. Currently, the catalysts more used in biodiesel production are the organic acids, such as the derivatives of toluene sulfonic acid and more often, mineral acids such as sulfuric acid. Although transesterification using acid catalysts is much slower than that obtained from alkali catalysis, typically 4000 times, if high contents of water and FFAs are present in the vegetable oil, acid-catalyzed transesterification can be used [10]. The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 2.2. It can be extended to di- and triglycerides. The protonation of carbonyl group of the ester leads to the carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst [9].

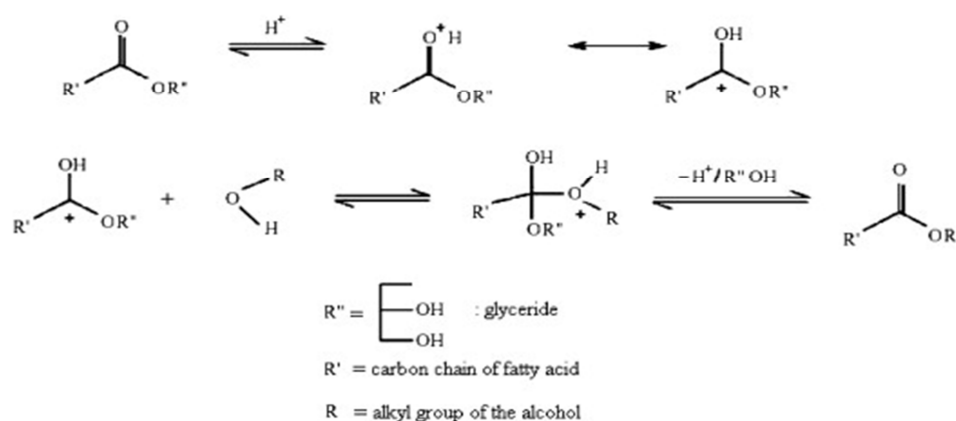


Figure 1. Mechanism of the acid-catalyzed transesterification [9].

F. Alkali-catalytic transesterification methods

The transesterification process is catalyzed by alkaline metal alkoxides, and hydroxides, as well as sodium or potassium carbonates [11]. Alkaline catalysts have the advantages, e.g. short reaction time and relatively low temperature can be used with only a small amount for catalyst and with little or no darkening of color of the oil.

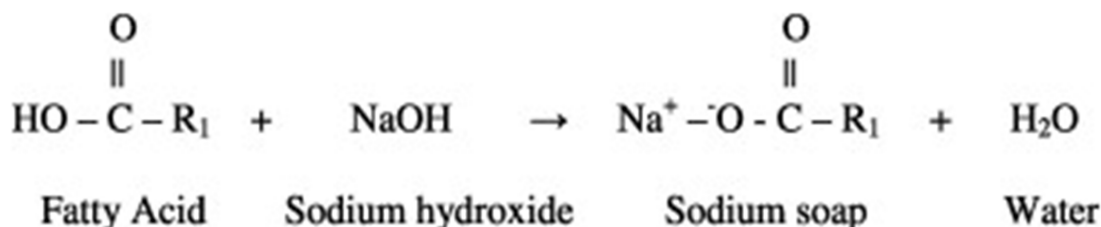


Figure 2. Formation of soap and water [24]

G. Mechanism of CaO catalyzed reaction

Many different studies reported the reaction mechanism of CaO-catalyzed transesterification, as for example articles of the proposed mechanism are shown in Figure 2.

As shown in Figure 1., the reaction begins with the attack of a methoxide ion, attached to the catalyst surface, to the carbonyl carbon of the triglyceride molecule to form a tetrahedral intermediate. In the second step, the unstable tetrahedral intermediate is rearranged and broken down to diglyceride anion and fatty acid methyl ester. The diglyceride anion is then stabilized by a proton from the catalyst surface to form diglyceride and at the same time the active site at the catalyst surface is regenerated. Then, the methoxide anion attacks on another carbonyl carbon atom in diglyceride, forming another mole of methyl ester and monoglyceride [28].

These three steps are repeated until all three carbonyl centers of the triglyceride have been attacked by the methoxide ions to give one mole of glycerol and three moles of methyl esters. According to results of different investigations reported in literature the first and second step of complex process (reaction of triglyceride and methanol and formation of diglycerides and FAME, as well as, reaction of diglycerides with methanol in which monoglycerides and FAMEs are formed) are always much faster than reaction of monoglycerides and methanol producing the final amount of FAME and glycerol [11].

They show high performance for obtaining vegetable oils with high quality, but a question often arises; that is, the oils contain significant amounts of FFAs which cannot be converted into biodiesels but to a lot of soap as shown in Figure 1. These FFAs react with the alkaline catalyst to produce soaps that inhibit the separation of the biodiesel, glycerin, and water [24].

II. MATERIAL AND METHODS

A. Materials

Water bath, beakers, separating funnel, evaporation apparatus, Methanol, sulphuric acid, potassium hydroxide, crude palm-oil, sodium sulphate, transesterification reactor, thermometer and conical flasks.

B. Methods

1. CaO Catalyst preparation

Highly active CaO was prepared by the calcinations-hydration-dehydration treatment of the eggshell. The dried eggshell was reduced to the smallest size and calcined in a muffle furnace under static condition at 900 °C for 5 hours, this is believed to transformed the calcium species i.e. CaCO₃ and other substances in the eggshell in to CaO and can be denoted as eggshell – CaO – 900 [16].

2. Synthesis of CaO nanoparticles catalyst

A simple and cost effective synthetic route was adopted for the synthesis inorganic metal oxide nanoparticle using chemical co-precipitation. In this process drop by drop addition of an aqueous sodium hydroxide (NaOH) in 20 ml solution of a calcined chicken eggshell which resulted in the supersaturated aqueous solution of CaO, under vigorous stirring at 60 °C on a magnetic stirrer for 60 minutes. This form a colloidal solution of calcium hydroxide (Ca(OH)₂). The obtained white colloidal solution of calcium hydroxide

(Ca(OH)₂) was washed in an alcoholic suspension to remove sodium and enhanced its stability due to a lower degree of agglomeration. The resulting suspension was passed across 125 mm Whitman filter paper and dried at 60 °C in an oven for 4 hours. These nanoparticles were then stored in a desiccator box for use. The ionic equation of the reaction can be predicted to be as follow;

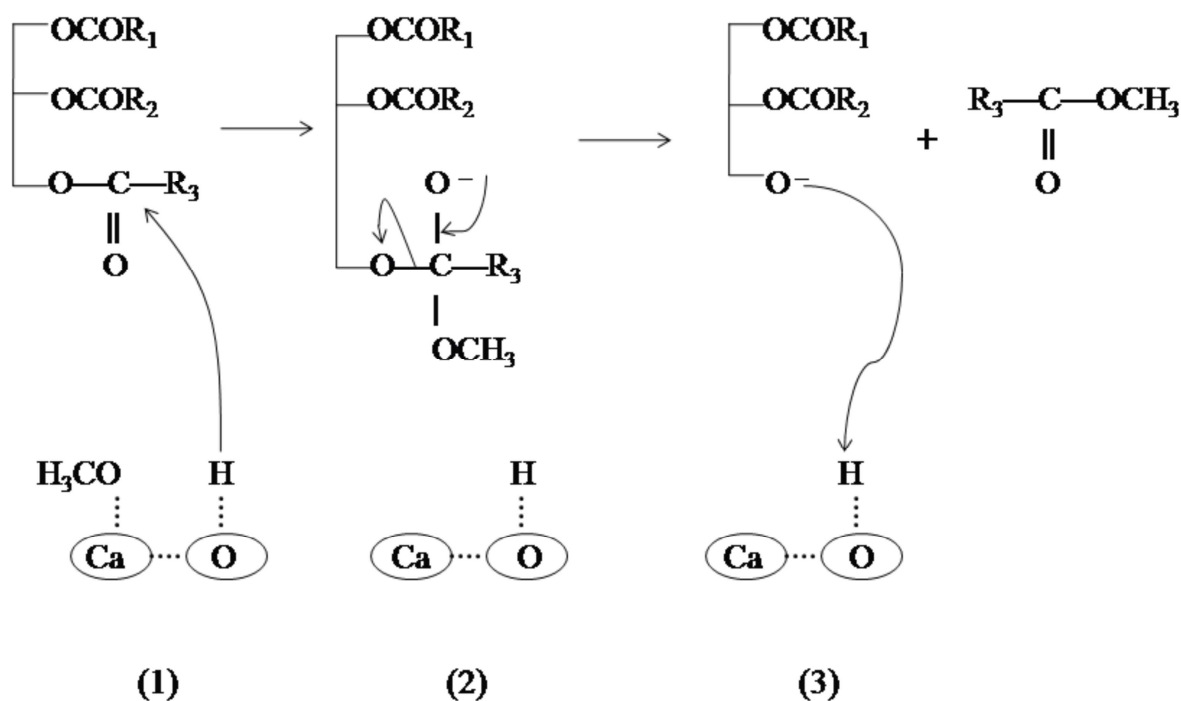
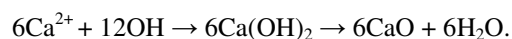


Figure 3. Mechanism of CaO-catalyzed transesterification [28].

III. RESULTS AND DISCUSSION

Table 2. Yields of Biodiesel (Two-step transesterification)

Run	Factor 1. A:Cat.con. w/w%	Factor 2. B:M.R	Factor 3. C:Temp. °C	R.I. Yield. %
1	3	10	50	59
2	1.75	6	55	61
3	3	6	60	62
4	1.75	8	55	76
5	1.75	8	50	73
6	1.75	10	55	65
7	3	10	60	61
8	1.75	8	55	76

9	1.75	8	55	76
10	0.5	8	55	67
11	0.5	6	50	65
12	0.5	10	50	68
13	1.75	8	55	76
14	1.75	8	55	76
15	1.75	8	60	80
16	3	8	55	58
17	0.5	6	60	59
18	3	6	50	60
19	0.5	10	60	69
20	1.75	8	55	76

A. Data Analysis

The statistical analysis of variance (ANOVA) was carried out using the software (Design-Expert 12 software – the latest version (Stat-Ease Inc., USA) so as to evaluate the precision of the model, the fitness and the significance of the model, the effects of the individual parameters and interaction effects on the response. In accordance with the results obtained using the ANOVA Table 2. the model was significant with a p-value less than 0.0001. Additionally, the Model F-value of 9.01 implies that the model is significant. In addition, Catalyst concentration A, Ethanol to Oil molar ratio B and the reaction temperature C, reaction temperature – catalyst concentration interaction, CA, and the interaction term of molar ratio – catalyst concentration, BA, were significant model terms with The lack of fit is regarded as the weighted sum of squared deviations between the mean response at each factor level and the corresponding fitted value [11]. In this research work the lack of fit is not significant for the response with a P-value of 0.0500 (lack of fit is 11); this indicates that the model is fitted to all data (Not-significant, lack of fit is good). Adequate precision is a measure of signal to noise ratio; it compares the range of the

predicted values at the design points to the average prediction error and as prerequisite of the model, a ratio of greater than 4 is desirable. In this model, the ratio of 13.058 indicates sufficient model discrimination.

B. Development of Regression Model Equation

The complete design matrixes together with both the experimental as well as predicted values obtained for yield response at the design points are shown in Table 2. The runs at the center points were used to determine the experimental error. Biodiesel yield obtained ranged from 58.00% to 80.00%. A polynomial regression equation was developed by using CCD coupled with RSM to analyze the factor interactions by identifying the significant factors contributing to the regression model. Design-Expert software (version 12 – latest) fitted four models to the response: linear, two factor interaction (2FI), quadratic and cubic polynomials. According to the sequential model sum of squares, the best model was selected based on the highest order polynomial where the additional terms were significant and the model was not aliased.

C. Build Information

File Version	12.0.0.6		
Study Type	Response Surface	Subtype	Randomized
Design Type	Central Composite	Runs	20
Design Model	Quadratic	Blocks	No Blocks
Build Time (ms)	7.00		

Table 3. Factors

Factor Name		Units	Type	Min.	Max.	Coded Low	Coded High	Mean	Std. Dev.
A	Cat.con	w/w%	Numeric	0.50	3.00	-1 ↔ 0.50	+1 ↔ 3.00	1.75	0.98
B	Molar ratio		Numeric	6.00	10.00	-1 ↔ 6.00	+1 ↔ 10.00	8.00	1.45
C	Temp	°C	Numeric	50.00	60.00	-1 ↔ 50.00	+1 ↔ 60.00	55.00	3.63

Table 4. Responses

Response Name	Units	Observations	Analysis	Minimum	Maximum	Mean	Std. Dev.	Ratio	Transform	Model
R1	Yield %	20	Polynomial	58	80	68.15	7.37	1.38	None	Quadratic

Table 6. Matrix Measures

Description	Value
Condition Number of Coefficient Matrix	1.00
Maximum Variance Mean	0.35
Average Variance Mean	0.15
Minimum Variance Mean	0.05
G Efficiency	57.14
Scaled D-optimality Criterion	1.68
Determinant of $(X'X)^{-1}$	5E-5
Trace of $(X'X)^{-1}$	0.35
I (Cuboidal)	0.15

If the condition number is 100-1000, there is moderate to strong multicollinearity. Values above 1000 indicate severe multicollinearity.

The determinant, trace, and 'I' values can only be used when comparing designs with the same number of runs. A smaller value is better.

When comparing designs, a smaller Scaled D-optimality Criterion is better.

Table 7. ANOVA for Quadratic model

Response 1: Yield

Transform: Natural Log

Constant: 0

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	0.23	9	0.0223	9.67	0.0007 significant
A-Cat.con	0.0194	1	0.0194	8.41	0.0158
B-Molar ratio	0.0054	1	0.0054	2.34	0.1570
C-Temp	0.0006	1	0.0006	0.2473	0.6297
AB	0.0069	1	0.0069	2.99	0.1143

AC	0.0028	1	0.0028	1.20	0.2998
BC	0.0016	1	0.0016	0.6812	0.4284
A ²	0.0460	1	0.0460	19.97	0.0012
B ²	0.0391	1	0.0391	16.98	0.0021
C ²	0.0152	1	0.0152	6.61	0.0278
Residual	0.0230	10	0.0023		
Lack of Fit	0.0230	5	0.0046		
Pure Error	0.0000	5	0.0000		
Cor Total	0.2234	19			

Table 8. Coefficients in Terms of Coded Factors

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	4.30	1	0.0165	4.27	4.34	
A-Cat.con	-0.0440	1	0.0152	-0.0778	-0.0102	1.0000
B-Molar ratio	0.0232	1	0.0152	-0.0106	0.0570	1.0000
C-Temp	0.0075	1	0.0152	-0.0263	0.0413	1.0000
AB	-0.0293	1	0.0170	-0.0671	0.0084	1.0000
AC	0.0185	1	0.0170	-0.0192	0.0563	1.0000
BC	0.0140	1	0.0170	-0.0238	0.0518	1.0000
A ²	-0.1293	1	0.0289	-0.1937	-0.0648	1.82
B ²	-0.1192	1	0.0289	-0.1837	-0.0547	1.82
C ²	0.0744	1	0.0289	0.0099	0.1389	1.82

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multicollinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable.

D. Final Equation in Terms of Coded Factors

The equation 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 are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

E. Final Equation in Terms of Actual Factors

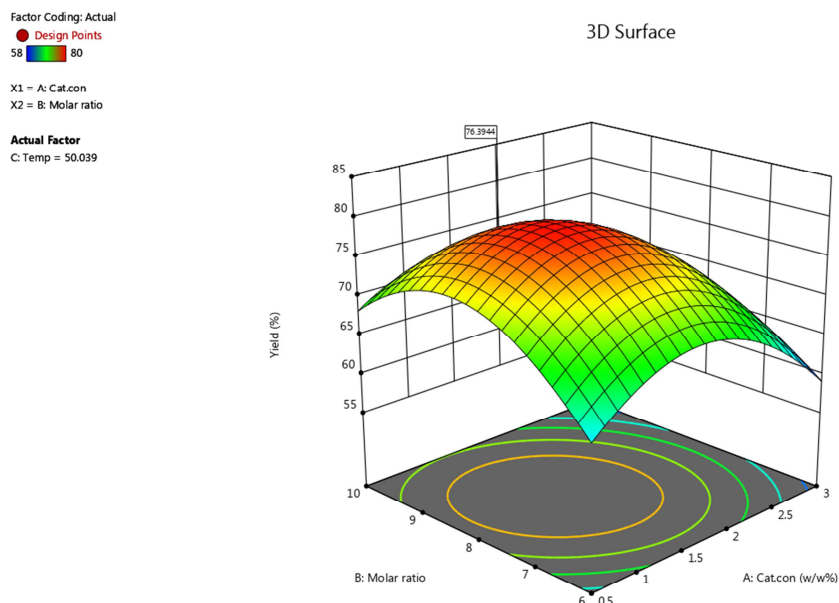
$$\begin{aligned} \ln(\text{Yield}) = & \\ & +11.76809 \\ & +0.185068 \text{ Cat.con} \\ & +0.431993 \text{ Molar ratio} \\ & -0.342253 \text{ Temp} \\ & -0.011738 \text{ Cat.con} * \text{Molar ratio} \\ & +0.002968 \text{ Cat.con} * \text{Temp} \\ & +0.001400 \text{ Molar ratio} * \text{Temp} \\ & -0.082735 \text{ Cat.con}^2 \\ & -0.029803 \text{ Molar ratio}^2 \\ & +0.002976 \text{ Temp}^2 \end{aligned}$$

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation will not be used to determine the relative impact of each factor because the

coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

To ascertain the reliability of the model, the data achieved predicted with reasonable accurateness by the

model in comparison with the experimental data. The figure below represents the predicted and the experimental value for the two-steps transesterification process using the developed model equation.



Figures 4a: Plots (3D) for Response surface presenting the effects of molar ratio and cat. conc (%), on the yield of biodiesel at constant time.

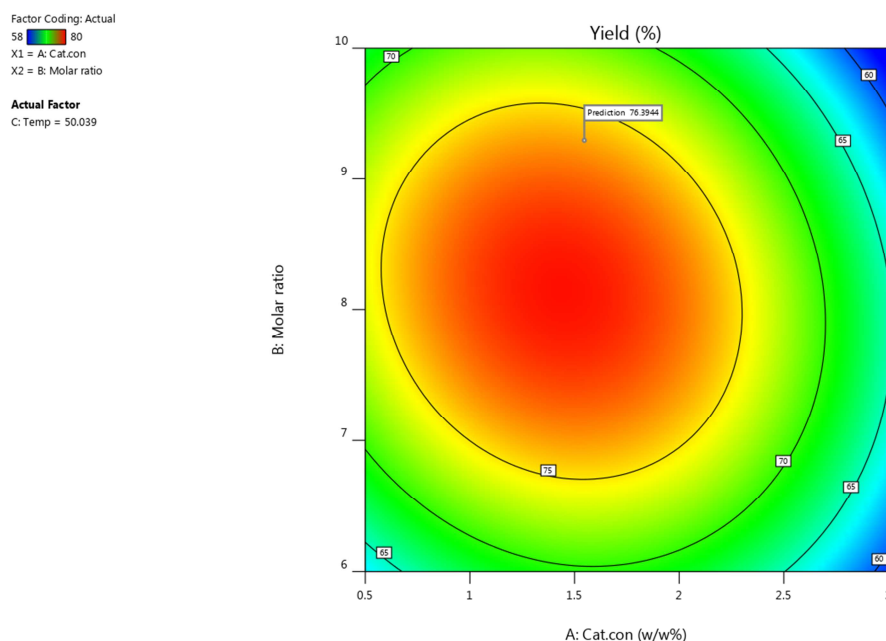


Figure 4b: Plots (2D) for contour presenting the effects of molar ratio and cat. Conc (%) on the yields of biodiesel at constant time.

F. Influence of the Parameters on the Methyl Ester Yields

Based on the developed models, it was observed that all the three parameters (A, B, and C) played a vital role during the production of biodiesel via two-steps transesterification. Surface plots of the predicted methyl ester yields, which can be generated by either Equation (1).

For Figures 4 (a) and (b), it can be shown that, at 55 – 57 °C reaction temperatures, the amount of methyl ester yields increased with the same reaction time. However, low biodiesel yields were recorded at temperatures of 60 °C, which could be attributed to the volatility of methanol as it approaches its boiling point. It is worthy to mention that high biodiesel yields were achieved at a reaction of 70 min.

G. Process of Optimization

There are abundant technologies obtainable for the optimization of chemical processes. Based on the predicted models, numerical hill-climbing algorithms were employed to seek for the most desirable outcome. Numerical optimization provides up-to-date and a complete description of the most effective methods in continuous optimization. It responds to the growing interest in optimization in business, science, and engineering by focusing on the technologies that are most suited to practical problems [2] [11]. Thus the optimization process was performed based on the limits of

parameters and response generated for the transesterification; consequently, the optimum conditions are catalyst concentration (A) is 1.75 ww%, Methanol to oil ratio (B) is 1:8 and Temperature for the reaction (C) is 60 °C, these are the optimum conditions which produces the highest yield of 80%. At these optimum points, the value of biodiesel yields almost meets the condition specified by EN 14214 (96.00 %). Good agreement between the results achieved for the experimental and predicted values established the validity of the models and the existence of the optimum condition. Further the accuracy of the models can be further justified by p-values presented in the ANOVA Table 7. In addition, the results obtained demonstrated that Response Surface Methodology (RSM) with appropriate design of experiment can be successfully applied for the optimization of the parameters in a production process. Therefore, this study is centered on the application of RSM to optimize biodiesel yield via two-step heterogeneous-catalyzed transesterification reaction. The optimization process may present valuable information pertaining to the development of efficient and economic processes for the production of biodiesel using transesterification process.

Table 9. Factors

Factor	Name	Level Low	Level High	Level Std. Dev.	Coding
A	Cat.con	1.55	0.5000	3.00	0.0000 Actual
B	Molar ratio	9.30	6.00	10.00	0.0000 Actual
C	Temp	50.04	50.00	60.00	0.0000 Actual

Table 10. Point Prediction

Two-sided Confidence = 95% Population = 99%

Solution 1 of 100 Response	Predicted Mean	Predicted Median*	Observed	Std Dev	SE Mean	95% CI low for Mean	95% CI high for Mean	95% TI low for 99% Pop	95% TI high for 99% Pop
Yield†	76.3944	76.3065		3.66719	N/A	70.9334	82.2758	59.0013	98.6874

For transformed responses the predicted mean and median may differ on the original scale.

Table 11. Confirmation

Two-sided Confidence = 95%

Solution 1 of 100 Response	Predicted Mean	Predicted Median*	Observed	Std Dev	n	SE Pred	95% PI low	Data Mean†	95% PI high
Yield‡	76.3944	76.3065		3.66719	1	N/A	66.9972		86.9093

For transformed responses the predicted mean and median may differ on the original scale.

Table 12. Confirmation

	Intercept	A	B	C	AB	AC	BC	A ²	B ²	C ²
ln(Yield)	4.303	-0.043	0.023	0.007	-0.029	0.018	0.013	-0.129	-0.119	0.074
p-values		0.015	0.157	0.629	0.114	0.299	0.428	0.001	0.002	0.027

IV. CONCLUSION

A sustainable biofuel has two favorable properties, which are availability from renewable raw material and its lower negative environmental impact than that of fossil fuels. Various vegetable oil extraction and transesterification technologies are currently used in the production of biodiesel fuel. As an alternative fuel, vegetable oil is one of the renewable fuels. However, twenty (20) different conditions were utilized whereby the yield of biodiesel varies from 58% to 80%. This clearly shows that CaO nanoparticle is a good catalyst for catalysis in production of biodiesel.

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