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Optimization Of Biodiesel Production From A Blend Of Used Cooking Oil And Jatropha Oil Using Solid Catalyst Synthesized From Natural Calcite

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Abstract

An efficient and highly active catalyst for the production of biodiesel was developed by subjecting calcite rock sample to calcination for 4 hours at 900 °C. The characteristics of the catalyst were evaluated using various analytical techniques such as X-ray fluorescence (XRF) and X-ray diffraction (XRD). The catalyst performance was evaluated through the transesterification of a blend of used cooking oil (UCO) and jatropha oil (50:50) to produce biodiesel in an optimization study using Box-Behnken design (BBD). The process conditions for the optimization study were reaction temperature, methanol: oil molar ratio, catalyst loading, and reaction time. The composition of calcite catalyst showed the presence of various oxides; CaO (65.276 %) was the main oxide present and this served as a basic oxide necessary for transesterification reaction to occur. Also present was 5.692 % of SiO_2 and 1.488 % of Al_2O_3 which is an amphoteric oxide. The catalyst performance for biodiesel production gave an optimum biodiesel yield of 80.12 % at optimal conditions of 2.95 wt% catalyst loading, 11.40:1 methanol: oil ratio, 49.88 °C reaction temperature, and a reaction time of 179.67 minutes. The GC-MS analysis, pour point, density, viscosity, flashpoint and cetane number of the produced biodiesel conformed to ASTM standards

1. Introduction

Since the 1970s, the output of energy derived from fossil fuels has surged rapidly to fulfil the world's need for transportation, heating, cooling, and power [1]. Since fossil fuel supplies are limited and take millions of decades to produce, they are not regarded as renewable energy sources. The widespread use of oil products in recent decades has led to environmental pollution, and numerous health issues for humans, such as cardiovascular diseases and cancer [2], [3], [4].

Biodiesel is getting traction as a reliable substitute due to its renewable nature, non-toxicity, superior fuel properties, including a higher cetane number, biodegradability, and eco-friendly benefits [5]. Advantages of using biodiesel include significant reductions in unburnt hydrocarbons, pollutants like SO_2 and CO, and particulate matter emissions [6], [7]. Producing biodiesel can be done in several ways, including direct usage or blending, transesterification, thermal cracking or pyrolysis, and micro-emulsion [4]. Among these, transesterification is notably efficient and manageable, involving the reaction of triglycerides with methanol, together with a catalyst to create glycerol and esters [8], [9]. Even while homogeneous catalysts are very active, they might produce unwanted

byproducts like soap when the feedstock contains a lot of water and free fatty acids (FFAs. This not only complicates product separation but also diminishes catalyst efficiency, necessitating a labour-intensive water-washing step [10]. In contrast, heterogeneous catalysts offer a solution to these issues. Various solid catalysts, such as ion-exchange resins, zeolites, solid-acids based on inorganic oxides, supported alkaline earth metals, supported noble metallic oxides, and alkaline earth oxides, have often been employed for biodiesel synthesis. A great deal of study has gone into solid catalysts for the methanol transesterification of vegetable or animal oil [11].

The use of heterogeneous catalysts promises to lower biodiesel production costs, thereby making it a more economically friendly alternative to petroleum-based diesel. Significant research has been devoted to synthesizing solid catalysts, highlighting their advantages over homogeneous catalysts, which is the focus of this study. Numerous renewable materials from natural sources, like eggshells, snail shells, and calcite, can serve as heterogeneous catalysts in the biodiesel production process [12].

Natural materials can provide cost-effective calcium oxide (CaO) sources and other metal oxides, serving as affordable heterogeneous catalysts. Calcium oxide is particularly promising due to its high basicity, low cost, low toxicity, and rapid reaction rate. During the reaction, it transforms into calcium methoxide and calcium glyceroxides [13], [12]. Calcium oxide has often been largely used as a heterogeneous catalyst in various studies, some of which focus on modifying calcite through hydration for biodiesel production [14], and optimizing production using a definitive screening design [12].

The Earth's crust is full of naturally occurring calcite rock, which is also sold commercially in significant quantities. It primarily consists of magnesium carbonate ($MgCO_3$), calcium carbonate ($CaCO_3$), and other compounds. To activate the active phase, calcite rock must be calcined to decompose into metal oxides like calcium oxide (CaO) and magnesium oxide (MgO) [15], [16]. These oxides are highly reactive in the methanolysis of vegetable oil and animal fats into fatty acid methyl ester (FAME), making them well-suited for biodiesel synthesis [17].
Using both edible oils for biodiesel production presents several challenges, including high feedstock costs, insufficient quality, competition with food supplies, and limited availability for large-scale production. To address these issues, researchers worldwide have proposed various strategies. One effective and low-cost method suggested is oil mixing before transesterification [15]. By blending bulk oils with poor fuel quality with those with better fuel properties in the right proportions, fuel quality can be improved [19], [20]. For example, in India, the anticipated availability of non-edible oils like Jatropha and Pongamia could be mixed with used cooking oil, which has good fuel properties, to enhance overall fuel quality [21].

This work aims to develop a highly effective and active heterogeneous catalyst from calcite rock sample and utilize it in the production of biodiesel from used cooking oil-jatropha oil Blend (UCJO), advancing research toward a more cost-effective and environmentally friendly biodiesel production process. The production process was optimized and modelled using the Response Surface Methodology (RSM) tool.

2. Materials and Methods

2.1 Materials

Calcite rock samples were obtained from Ikpeshi, Edo State, Nigeria. The used cooking oil was collected from local Restaurants and Eateries around the University community, Ugbowo, Edo State, Nigeria. The Jatropha oil was bought from Delta State, Nigeria. Other reagents used, such as

methanol, potassium hydroxide, benzene, sulfuric acid and ionized water were all of standard grade manufactured by BDH UK.

2.2 Methods

2.2.1 Catalyst Preparation

The collected raw calcite rock was placed in a clean polythene bag. The calcite rock sample was then crushed to reduce the particle size and sieved through a 100mm mesh sieve. 200g was taken from the sieved calcite, and calcined at 900℃ in a muffle furnace for 4 hours [22]. The organic materials and metal carbonates were to be broken down into their oxides by heat treatment. After that, the catalyst, or calcined calcite, was kept in a desiccator. To determine the metallic compositions and crystalline phases of the catalyst, the samples were analyzed using XRD and XRF techniques.

2.2.2 Oil Preparation

The collected used cooking oil (UCO) was sieved to remove any food particles present. The sieved UCO was then blended with Jatropha oil in a ratio of 50:50 by volume. The oil blend obtained from a mixture of UCJO and Jatropha oil had a high free fatty acid (FFA), thereby necessitating esterification to reduce the FFA value. 2g of Sulfuric acid and 44g of methanol was added to 200g of the oil sample. The mixture was stirred for 90 minutes using a hot plate magnetic stirrer at 60℃. At the completion of the process, the mixture was poured into a separating funnel and given an hour to separate. The surplus methanol was carefully separated from the esterified oil.

2.2.3 Biodiesel Production and Characterization

The process of transesterification of UCJO using calcite catalyst involved weighing 50g of UCJO placed on a hot plate magnetic stirrer, and heated to a specified temperature. Then, a specified amount of calcite catalyst and methanol was added to the mixture and allowed to react for a specified duration (as specified by the design of experiment (DOE)). A constant agitation rate of 100 rpm was maintained throughout the reaction. These experimental conditions were determined using a Box-Behnken Design (BBD) so as to optimize the reaction parameters.

Catalyst and mixture were separated at the conclusion of each reaction time. The glycerol and biodiesel were then allowed to separate overnight by pouring the mixture into a separating funnel. To guarantee that all contaminants were eliminated, the biodiesel was thoroughly washed three times with hot, distilled water. After being washed, the biodiesel went through drying in an oven. Equation (1) was used to compute the biodiesel yield.

$$\%Yield = \frac{Grams\ of\ biodiesel\ produced}{Grams\ of\ oil\ used} \times 100 \quad (1)$$

The biodiesel produced from the oil sample is characterized to get the viscosity, density and pour point and compared with ASTM standard.

2.3 Design of Experiment (DOE) for Biodiesel Optimization

The biodiesel production process was optimized using the Response Surface Methodology (RSM) with Design Expert 13. The Box-Behnken design (BBD) was used to determine the response, specifically the percentage yield of biodiesel in response to the various independent input process variables. These input variables are the catalyst loading (wt.%), methanol-to-oil ratio (mol/mol), temperature (°C), and time of reaction (minutes).

Table 1 illustrates the selected variables and their respective levels for optimizing the biodiesel synthesis process:

Table 1: Optimization input variables

Factors	Units	Lower level	Upper level
Temperature (A)	^oC	45	65
Catalyst loading (B)	Wt. %	1	3
Methanol-oil ratio (C)	Mol/mol	6	12
Time of reaction (D)	Minutes	60	180

3.0 Results and Discussion

3.1 Characterization of Oil Blend

Table 2: Characterization result of the oil blend

Parameters determined	Unit	Value		
		Jatropha oil	Used Cooking oil	Oil Blend (50:50)
Acid Value	mgKOH/g	15.08	4.12	10.94
Free Fatty Acid Content	Wt.%	7.54	2.06	5.47
Saponification Value	mgKOH/g	208.45	197.4	204.77
Peroxide Value	(mEqO2/g)	-	-	2.45
Iodine Value	mgL2/100g	15.228	13.705	12.182
Density	g/mL		0.933	0.952
Moisture content	%	0.1	1.5	1.0
Viscosity	(MPa.S)	62.8 (at 31.1^{o}C)	66.7 (at 31.1^{o}C)	18.1 (at 31.1^{o}C)

Table 2 shows that the oil blend's acid value is 10.94 mg KOH/g, corresponding to an FFA content of 5.47 wt.%, which is too high for biodiesel production [8], [23]. This high FFA level necessitates acid esterification before transesterification [24]. This pretreatment reduced the FFA to 1.12 wt.%, making it suitable for transesterification [23]. Despite both oils having high FFA content, blending helps balance fatty acid composition, improve oxidative stability, and enhance overall fuel properties [25].

3.2 Catalyst Characterization

3.2.1 X-ray Diffraction Analysis

The structural analysis of the catalyst was determined by X-ray Diffraction (XRD), which is a highly effective method for elucidating the crystal structure of materials. Figure 1 illustrates the XRD pattern of the calcined calcite catalyst, there are sharp peaks representing CaO at 2Θ =32.377 ^{o}, 37.478 ^{o}, 53.997 ^{o}, 64.248 ^{o} and 67.533 $^{o;}$ indicating a crystalline structure. It should be noted that CaO is the main component facilitating the transesterification reaction

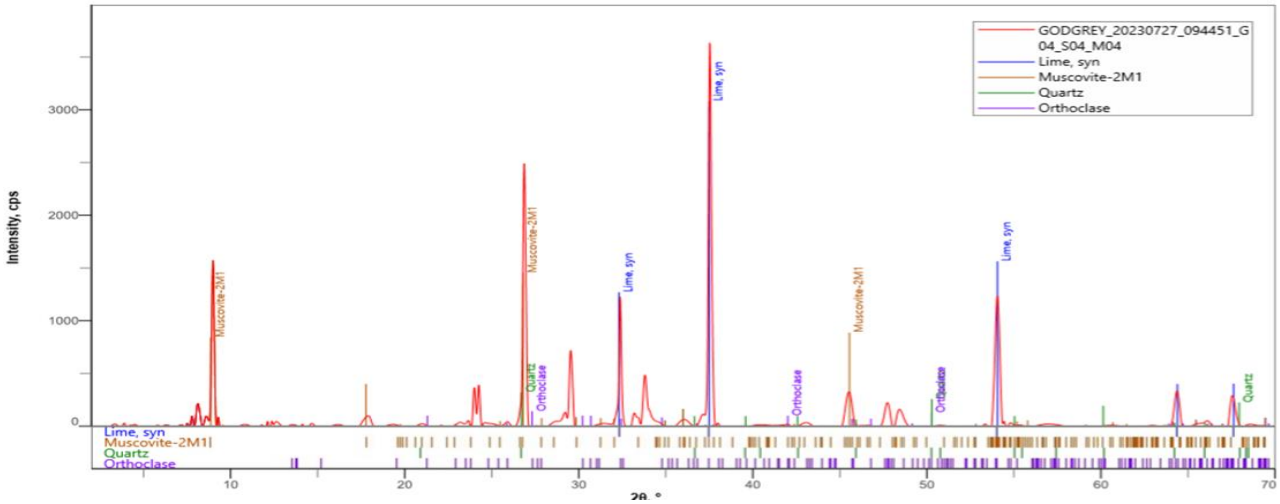


Figure 1: XRD analysis result of calcined calcite

3.2.2 X-ray Fluorescent Analysis

Table 3 shows the composition of the various oxides present in the catalyst. CaO made up 65.276 % of the entire oxide present in the catalyst and is the main oxide needed for the transesterification reaction. Also present is 5.692 % of SiO_2 and 1.488 % Al_2O_3 which is an amphoteric oxide. The high content of CaO in the sample indicates that the calcination of the raw calcite was relatively successful.

Table 3: Oxides of Calcined catalyst

Oxides	Concentration (%)
Fe_2O_3	0.3027
ZnO	0.00240
Ta_2O_5	0.00046
MgO	2.42
Al_2O_3	1.488
SiO_2	5.692
P_2O_5	0.0550
SO_3	0.7481
Cl	0.0114
K_2O	0.7846
CaO	65.276
TiO_2	0.0297
MnO	0.0363
BaO	0.47029
SrO	7.148
Nb_2O_5	0.1246
PbO	0.00191

3.3 Response Surface Methodology Optimization

The actual and predicted percentage yields of biodiesel after 29 experimental runs as specified by the design are shown in Table 4 along with the transesterification experimental design matrix.

Table 4: RSM Box-Behnken Design Matrix result

Run	Methanol/oil ratio (mol/mol)	Catalyst loading (wt.%)	Reaction temperature (°C)	Reaction time (min.)	Experimental yield (%)	RSM Predicted yield (%)
1	6	2	55	60	62.1	61.85
2	9	2	55	120	68.23	68.92
3	6	1	55	120	58.2	57.84
4	9	2	55	120	65.7	68.92
5	9	2	45	60	55.8	56.78
6	6	2	65	120	62.01	62.22
7	6	2	45	120	58.1	57.61
8	9	2	55	120	70.1	68.92
9	9	1	55	180	60.1	59.61
10	9	3	55	60	57.2	56.85
11	9	2	45	180	64.13	64.80
12	9	2	55	120	70.01	68.92
13	9	2	55	120	70.56	68.92
14	9	1	65	120	56.6	57.58
15	9	3	45	120	61.56	61.24
16	9	3	55	180	74.4	73.65
17	12	2	65	120	70.12	69.77
18	9	1	45	120	55.82	56.03
19	9	3	65	120	65.45	65.90
20	6	2	55	180	60.89	61.34
21	12	2	55	180	79.52	80.43
22	9	1	55	60	57.44	57.36
23	12	2	45	120	69.22	68.17
24	12	2	55	60	60.67	60.88
25	12	1	55	120	63.6	63.34
26	6	3	55	120	60.6	61.04
27	12	3	55	120	73.13	73.67
28	9	2	65	180	70.21	69.41
29	9	2	65	60	58.87	58.38

3.3.1 Model Summary Statistics

The optimal model that is statistically significant and best captures the link between input variables and the response (biodiesel production) of the transesterification reaction process was found by an analysis using quadratic, cubic, linear, and two-factor interaction (2FI) models. Table 5 indicates that the quadratic model gave a higher **R^2** for both the predicted and adjusted yield than that of the cubic model. Hence, the quadratic model is suggested for analyzing the result. The R^2, R^2 adjusted and R^2 predicted values obtained were 0.9784, 0.9568 and 0.9365 respectively, indicating the model's suitability

Table 5: Model Statistics

SOURCE	STD. DEV.	R^2	ADJUSTED R^2	PREDICTED R^2	PRESS	
Linear	4.20	0.6178	0.5541	0.4590	599.68	
2FI	3.73	0.7740	0.6484	0.5129	539.90	
Quadratic	**1.31**	**0.9784**	**0.9568**	**0.9365**	**70.39**	**Suggested**
Cubic	1.75	0.9834	0.9224	0.6748	360.51	Aliased

3.3.2 Analysis of variance (ANOVA) for the response surface quadratic model

ANOVA helps to determine whether the different factors being examined (temperature, time, methanol ratio, catalyst loading) have a statistically important impact on the yield of biodiesel. By analyzing the p-values shown in Table 6 associated with each factor, you can identify which factors have a meaningful effect on the yield of biodiesel.

Table 6: ANOVA for the response surface quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1084.47	14	77.46	45.25	< 0.0001	Significant
A- Temperature	28.92	1	28.92	16.90	0.0011	
B- Catalyst Loading	137.23	1	137.23	80.17	< 0.0001	
C- Methanol	246.25	1	246.25	143.86	< 0.0001	
D-Time	272.37	1	272.37	159.12	< 0.0001	
AB	2.42	1	2.42	1.41	0.2544	
AC	2.27	1	2.27	1.32	0.2693	
AD	2.27	1	2.27	1.32	0.2693	
BC	12.71	1	12.71	7.42	0.0164	
BD	52.85	1	52.85	30.88	< 0.0001	
CD	100.60	1	100.60	58.77	< 0.0001	
A^2	110.62	1	110.62	64.62	< 0.0001	
B^2	137.45	1	137.45	80.30	< 0.0001	
C^2	0.7758	1	0.7758	0.4532	0.5118	
D^2	38.92	1	38.92	22.74	0.0003	
Residual	23.96	14	1.71			
Lack of Fit	7.85	10	0.7849	0.1948	0.9836	not significant
Pure Error	16.11	4	4.03			
Cor Total	1108.44	28				
Fit Statistics						
Std. Dev.	1.31		R^2	0.9784		
Mean	64.15		Adjusted R^2	0.9568		
C.V. %	2.04		Predicted R^2	0.9365		

An indication of the model's relevance is its 45.25 Model F-value. An F-value this large could very well be the product of random variation with a mere 0.01% chance. Concerning the F-value for Lack of Fit, which is 0.19, it indicates that, in comparison to pure error, the Lack of Fit does not exhibit statistical significance. About 98.36% of the time, there is a strong probability that random fluctuation might produce a Lack of Fit F-value this large. Essentially, it is favorable when there is a non-significant lack of fit since it indicates that the model fits well.

P-values less than 0.05 implies significant model terms. Here, the model terms A, B, C, D, BC, BD, CD, A^2, B^2, and D^2 are significant.
The statistical data indicate that the R^2 and adjusted R^2 values were 0.9784 and 0.9568, respectively. The small difference of less than 0.2 between these values indicates that the predicted R^2 and adjusted R^2 are closely aligned. Therefore, this model can be used for theoretical predictions in the biodiesel production process.

3.3.3 Model Equation
The model in terms of the coded factors is shown in the equation 2;

$$Yield = +68.92 + 1.55A + 3.38B + 4.53C + 4.76D + 0.7775AB - 0.7525AC + 0.7525AD + 1.78BC + 3.63BD + 5.01CD - 4.13A^2 - 4.60B^2 - 0.3458C^2 - 2.45D^2 \quad (2)$$

Representations of the equation in terms of coded factors enable the prediction of the response at particular levels of each factor. Generally, the high levels of factors are represented by +1 in this depiction, while the low levels are represented by -1. By looking at and comparing the coefficients of various elements, this coded equation is a useful tool for determining the relative impacts of various factors

3.3.4 Plot of actual vs predicted
Figure 2 shows the actual vs predicted plot, indicating an excellent fit between experimental values and the expected values as indicated by the model.

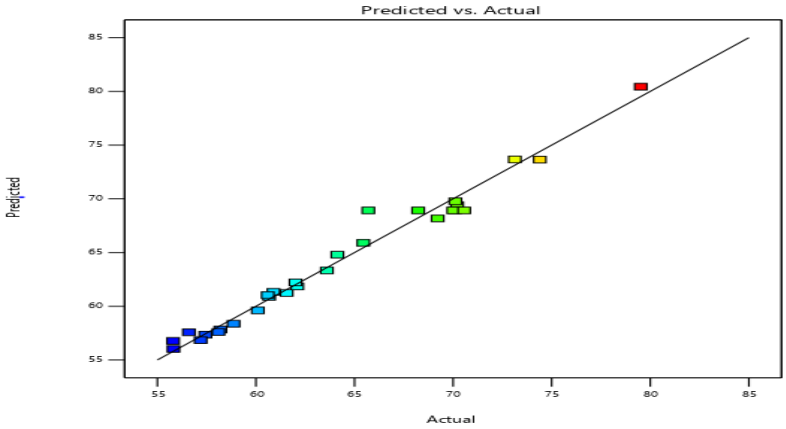
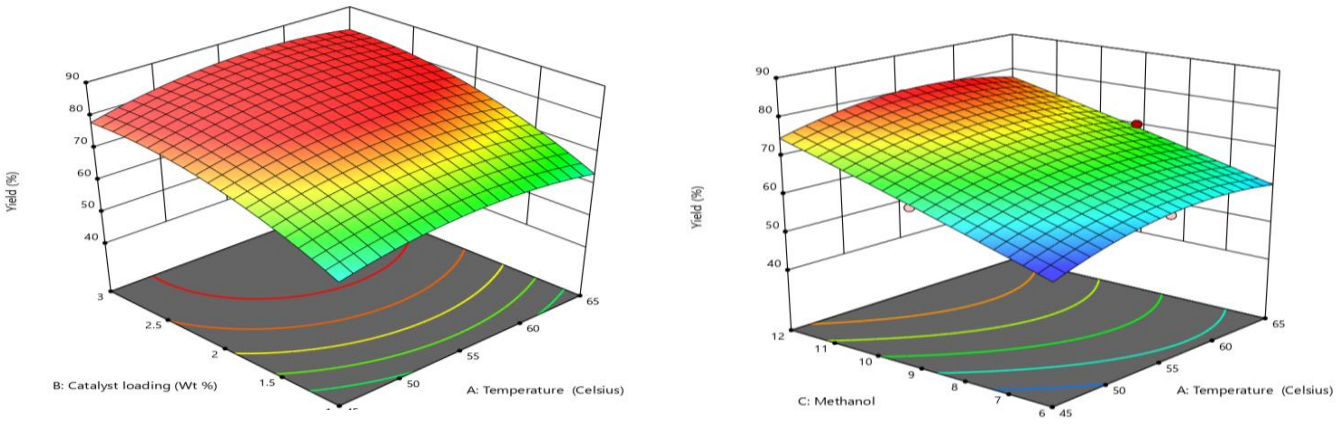


Figure 2: Actual vs Predicted yield

3.3.5 Effect of interaction of transesterification input variables on biodiesel yield
The significance of the model terms AB, AC, AD, BC, BD, and CD was assessed through the examination of three-dimensional (3D) surface plots as shown in the figure 3.



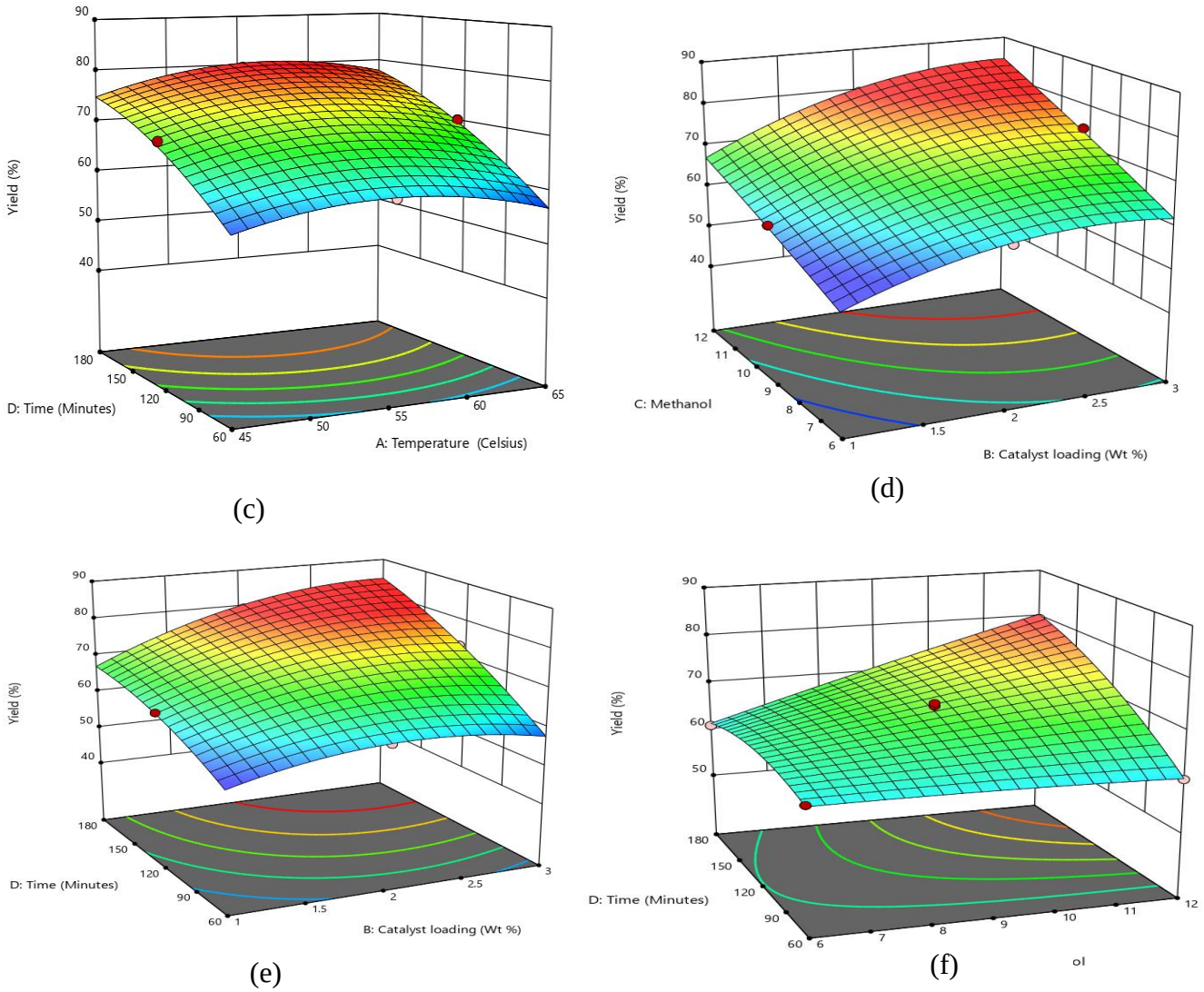


Figure 3: 3D plots showing the interaction between (a) Temperature and catalyst loading (b) Temperature and methanol ratio (c) Temperature and time (d) Catalyst loading and methanol ratio (e) Catalyst loading and time (f) Methanol ratio and time

3.3.6 Numerical optimization and model validation

The model generated was used to explore the design space and identify factor settings that align to maximize the biodiesel yield. Among the numerous solutions generated, over 100 in total, the optimal values were chosen based on the highest desirability score and they are a catalyst loading of **2.950 wt%,** reaction temperature of **49.88**^{o}C, methanol to oil ratio of **11.40** and reaction time of **179.67minutes**. These conditions combined gave a biodiesel yield of **80.125%.** Using the optimum parameters value experimentally repetitively for a three times, an average yield of 80.62% was obtained. The close correlation between the predicted value (80.125%) and experimental value (80.62%) confirmed the validity of the response model.

3.4 Characterization of Biodiesel produced

3.4.1 GC-MS Analysis of Biodiesel Produced

Figure 4 shows the GC-MS analysis of the produced biodiesel. Six (6) major peaks were observed using GC-MS to analyze the chemical composition of the produced biodiesel, and Library match software (NO. NIST14) was used for the identification of each peak that corresponds to a fatty acid

methyl ester (FAME). The chromatogram showed the presence of Dodecanoic acid, 10-methyl-, methy ester with a retention time of 7.064 at peak 3, peak 6 showed the presence of Pentadecanoic acid, 14-methyl-, methyl ester with a retention time of 7.522, peak 9 showed the presence of 10,13-Octadecadienoic acid, methyl ester with a retention time of 8.111, peak 11 showed the presence of 9-Octadecenoic acid with a retention time of 8.111, peak 14 showed the presence of cis-11-Eicosenoic acid, methyl ester with a retention time of 8.740 and peak 18 showed the presence of 4,7,10,13,16,19-Docosahexaenoic acid, methyl ester with a retention time of 9.169

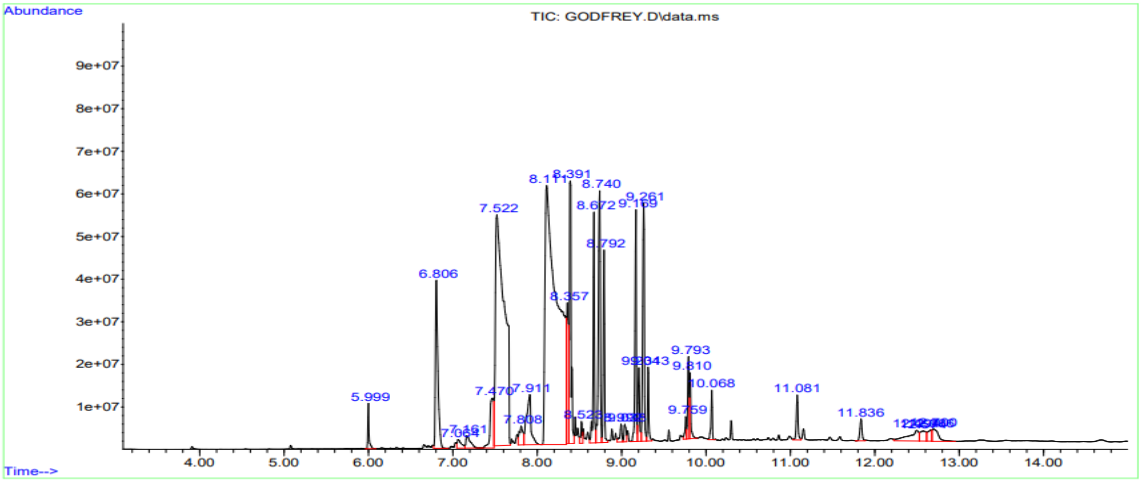


Figure 3: GC-MS analysis result

The FAME identified by GC-MS analysis were similar to that identified by [26] who produced biodiesel from non-edible oil using copper-modified clay catalysts. The identified FAME included both saturated and unsaturated.

3.4.2 Properties of biodiesel produced

Table 7 shows the properties of biodiesel produced in comparison with ASTM standards.

Table 7: Properties of Biodiesel Produced

Parameters Determined	Unit	Value	ASTM Standard
Colour	-	Light brown	No specification
State	-	Liquid	No specification
Moisture content	%	0.018	$\leq$ 0.03
Density	g/ml	0.954	0.860 – 0.900
Viscosity	(MPa.s)	6 (at 31.1°C)	1.9 – 6.0
Pour point	°C	0.4 °C	-3 – 12
Flash point	°C	141	≥130
Cetane number	-	50	≥47

4.0 Conclusion

Biodiesel was produced from a blend of used cooking oil and Jatropha oil employing calcite as an effective solid catalyst. The characterization results of the catalyst indicated that calcite can be effectively used as a solid heterogeneous catalyst for biodiesel production. Also, RSM was successfully utilized for the prediction and optimization of the process variables for biodiesel production. The optimal biodiesel yield of 80.125% was obtained at a catalyst loading of 2.95wt.%, a temperature of 49.88°C, a reaction time of 179.67 minutes, and a methanol-to-oil ratio of 11.40%.

The biodiesel produced using the catalysts met the appropriate range when compared to ASTM standards.

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