International Journal of Frontiers in
Engineering and Technology Research
Journal homepage: https://frontiersrj.com/journals/ijfetr/
ISSN: 2783-0497 (Online)

(RESEARCH ARTICLE)

Check for updates

Effects of process parameters variations and optimization of biodiesel production from orange seed oil using raw and thermal clay as catalyst

Igri Omini Uket * and Hyginus Ubabuike Ugwu

Department of Mechanical Engineering, Michael Okpara University of Agriculture, Umudike, Umuahia, Abia P. M. B 7276, Umuahia Nigeria.

International Journal of Frontiers in Engineering and Technology Research, 2023, 05(01), 001–013

Publication history: Received on 20 June 2023; revised on 02 August 2023; accepted on 05 August 2023

Article DOI: https://doi.org/10.53294/ijfetr.2023.5.1.0018

Abstract

In this study, process parameters for the production of biodiesel from orange seed oil using raw and thermal clay as catalyst were analyzed using randomized optimal design. The design was a response surface method (full fractional factorial) which identified the various design points as being numerical and discrete. The process optimization was performed by varying five factors, each at two different levels. The process parameters: methanol to oil molal ratio (mol/mol), catalyst concentration (weight %), reaction time (minutes), temperature (°C) and agitation speed (revolution per minutes, rpm) were the independent variables (input), while the biodiesel yield (vol/vol) was the dependent variable (response) in the optimization process. The designed matrix, 3D (three dimensional) surface plots, contour plots and analysis of variance (ANOVA), was achieved using the Design Expert Software (version 12.0), the optimum biodiesel yield was predicted and experimented to ascertain the interactive effects of parameters. The correlating regression coefficient indicated the satisfactory performance of the model for the raw and thermal clay. The experimental/actual maximum optimal biodiesel yield for the biodiesel production from the orange seed oil using raw and thermal clay as catalyst was 79.53 and 94.58% v/v while the predicted biodiesel yield was 79.55 and 92.98% v/v. The set of conditions that caused these positive effects were established at Time of 150 minutes, Temperature 65 °C, methanol /sample molal ratio of 12:1, catalyst concentration of 3.0 wt. % and agitation speed at 300 rpm respectively. Thisresults shows agreement between the actual and predicted biodiesel yield. It can be concluded that the best biodiesel yield can be achieved using thermally modified clay as catalyst.

Keywords: Biodiesel; Production; Trans-esterification; Oil; Orange seeds (*Citrus sinesis*); Feedstock

1. Introduction

Due to the high demand of fossil fuels for energy and transportation, leading to the depletion of the ozone layer and the negative health hazards, research into alternative sources of energy which would not only substitute the conventional energy resource, but also keep the environment free from pollution were explored. At the center of this alternative energy resource was biodiesel, which is made from vegetable oils, animal fats or recycled greases using trans-esterification, esterification, batch process and pyrolysis. It can be used as a fuel for vehicles in its pure form, but it is usually used as a petro-diesel additive to reduce levels of particulates, carbon monoxide, and hydrocarbons from diesel-powered vehicles (Victor, 2017). Over dependence on fossil fuels for energy production is a major treat to the environment due to environmental pollution which has championed the search for the need of an alternative source of energy which will be less harmful to the environment. In 2016, Port Harcourt had an environmental treat in the form of black dust (soot) which is formed as a result of incomplete combustion of fossil fuels as a result of industrial actions, which affected the health of people in that locality. Researchers carried out various research and discovered that fuel can be gotten from plants (biofuel), mixed with diesel blends to become a biodiesel. A lot of feed stocks were considered.

* Corresponding author: Uket Igri

Vegetable oil is an essential feedstock for the production of biodiesel. Banerjee (2014), investigated on Bio-diesel production from orange peels (Citrus Senesis) as feedstock, it was obtained from the results that the optimal biodiesel yield was 93% under the conditions of 80-83 °C, 1:3 oil to ethanol mole ratio, 70 minutes reaction time and sodium hydroxide as catalyst. Bull and Obunwo, (2014); Mishra *et al*. (2015), studied the effect of homogeneous catalysts on biodiesel production from crude neem oil feed stock and cost analysis on the production of biodiesel. The maximum average yield of the biodiesel was 72 ± 2% from a reaction time of 75 minutes, a reaction temperature of 50 °C, and methanol to oil molar ratio of 4:5:1 and 1% KOH as alkaline catalysts. Biodiesel production from refined cotton seed oil (Onukwili *et al*. 2016),biodiesel production from shea-butter using response surface methodology, in which an optimal biodiesel production was achieved at an optimal yield of 92.16% under the conditions of 40 °C for reaction temperature, an agitation speed of 800 rpm and molar to oil ratio of 7:1, Ajala *et al*. (2016), studied the use of beef, sheep tallow, poultry oil gotten from animals and waste cooking oil as feed stocks for biodiesel production. Montefri and Obbard (2010); Zhang *et al*. (2003) stated that it will be of great importance if the feedstock will include soaptocks, acid oils, used cooking oils, animal fats, non- food vegetable oils and microorganisms such as algae. Zullaikah *et al*. (2005), produced biodiesel from rice bran oil, (Agbede 2012), extracted oil from three fruit seeds (mango, tangerine, African star) for their worthiness for production of biofuel, and (Savariraj *et al*. 2011), worked on reducing viscosity and increasing calorific value using mango seed oil. Ibifubara *et al*. (2014), discovered that WCO as a feed stock reduced biodiesel production cost by about 60 – 70 percent because the feedstock cost constitutes 70-95 percent of the cost of biodiesel production. It is thus needful according for them to promote the global use of biodiesel, low-cost non-edible oils and waste vegetable oils for utilization as feed stocks for producing biodiesels. Yousef *et al*. (2013) investigated the physico-chemical properties of two types of shahrodi grape seed oils (Lal and Khalili) which was extracted using Soxhlet method and petroleum ether as solvent. Variables such as fatty acid, peroxide value, soapy number, acidity, were placed on considerations. The experiments revealed that, Linoleic acid, fatty acid content was almost equal to 65.39% of all fatty acids which gives oxidation reaction resistance. It was concluded that, Lal variety was better than Khalili for oil content and for low peroxide value. Heydarzaeh *et al*. (2018), described an alternative energy for the replacement of fossil fuels which has been developed. Biodiesel synthesis as a renewable energy was derived in a continuous packed column reactor. Free fatty acids (FFA) were esterified with ethanol in a heterogeneous catalytic reaction. The catalytic reactor had great potential as FFA introduced to the top of column, flow down ward, reached to catalyst surface and interacted with ethanol on the active site. The ester product was instantaneously formed. In this catalytic reaction, effects of mass ratio of the free fatty acids to ethanol along with reaction temperature in the range of 150-250 °C were considered, as reaction temperature increased, esterification reaction was enhanced. From the data obtained it was concluded that optimal conditions of molar ratio 3:5 and temperature of 250 °C helped in conversion of 90% free fatty acids into ethyl esters. According to (Sirajudin *et al*. 2013), palm oil is a potential alternative energy source, which will possibly replace the non-renewable fossil fuels, such as gasoline, kerosene and diesel oil. During usage, biofuel produces low pollutants than fossil fuel. The research was conducted through a catalyst synthesis and the catalytic cracking process. The catalytic cracking process was accomplished in a fixed bed micro reactor with temperatures ranging from 350 – 500 °C and Nitrogen gas flow rates ranging from 100 –160 ml/min for a period of 120 min. It was discovered that at a temperature of 450 °C and a flow rate of 100ml/min nitrogen produced the highest yield of gasoline fraction of 28.87%, 16.70% kerosene and 1.20% diesel. It was proven that synthesized HZSM-5 catalysts met the standards of a catalyst in producing biofuel by the catalytic cracking of vegetable oils.

Important properties of the biodiesel like density, flash point, calorific value and viscosity have also been estimated (Banerjee, 2014). Orange seed were obtained from orange found in the family Rutaceae, these seeds have the ability to yield oil and have been underutilized for any industrial or commercial purpose. The research work deals with the extraction of bio-oil from orange seeds using Soxhlet extractor thereby converting it into biodiesel by transesterification method and the characterization of the bio-oil and biodiesel to obtain their physiochemical properties. Optimization was also carried out using response surface methodology of central composite design (CCD).

2. Materials and Methods

Orange fruits was purchased from vendors in Marian market, Calabar Municipality in bags. The orange seeds obtained from the parent fruits was air dried, sorted to remove impurities and was grinded using an industrial blender. 100g of grinded seeds was weighed into a semi-permable cotton material and placed into the timble of a 500ml Sohxlet extractor while 400ml n-hexane was measured into a 500ml flat bottom round flask. The Sohxlet with the extraction timble containing the sample in a semi-permable membrane was connected with the condenser which was fitted to the flat bottom round flask containing n-hexane. The oil was heated to 105 °C to remove the moisture content before starting the reaction. Methanol and NaOH were added to oil and 300 rpm stirring speed was used. The method used in the production of the biodiesel was trans-esterification process and the variables for the reaction were methanol to oil ratio (4:1, 6:1, 8:1, 10:1, 12:1), catalyst concentration (1, 2, 3, 4, and 5%), reaction time (30, 60, 90, 120 and 150 minutes), reaction temperature (35, 45, 55, 65 and 75 °C), and reaction speed (150, 200, 250, 300, 350 and 400 rpm). The biodiesel was washed with hot water and dispensed into a 250 ml beaker. It was heated at 105 °C to remove water molecules from the biodiesel. The biodiesel was allowed to cool and stored in calibrated specimen bottles. The glass reactor was set on a heating mantle with electromagnetic field which will enable the agitation effect of the stirring nob. Initially, the reactor was preheated to eliminate residual moisture. A reflux condenser with cold water circulating at the outer jacket was fitted to mid neck of the reactor. Mercury in glass thermometer held in plastic bung was fitted to the right neck of the reactor. The left neck of the reactor was left open initially for input of reactants (oil mixture, methanol and modified catalyst) after which it was closed. Calculated amount of 'methanol' and modified 'catalyst' was added in the amounts established for each experiment and pre-stirred for 10 minutes for proper dissolution after which, 50ml of oil mixture (orange seed oil) was added and the stirring system switched on also at the established 'speed', taking this moment as time zero of the reaction. Each reaction was allowed to last for the required 'time' at specific 'temperature'. After the methanolysis reaction finished, the trans-esterification product was allowed to stand for twelve (12) hours in a separating funnel for glycerol separation. The crude glycerol was removed through the funnel tap leaving the methyl esther, (biodiesel) behind. The biodiesel was washed with hot water and dispensed into a 250 ml beaker. It was heated at 100 °C to remove water molecules from the biodiesel. The biodiesel was allowed to cool and stored in metric specimen bottles.

3. Results and Discussion

3.1. Physiochemical Properties

Table 1 Physiochemical properties of the orange seed oil

Property	**Value**	**Property**	**Value**
Colour	Light yellow orange	Molecular weight	766.76
Density	0.927	Pour point	15.00
Specific gravity	0.843	Flash point	259
Saponification Value	220.10	Acid value	0.5049
Kinematic Viscosity	32.994	Cloud Point	19.50

Table 2 Catalysts characterization of the clay

Parameter	**clay**
Moisture (%)	0.04
Bulk Density (g cm^{-3})	0.688
pH	5.70
Surface Area (m^2 g^{-1})	655
Organic Carbon (%)	2.96
Organic Matter (%)	8.78
Volatile matter (%)	9.84
Particle Density (g $cm^{-3)}$	1.37
Total porousity (%)	50.97
Ash (%)	6.43

Table 3a ANOVA table for biodiesel production from orange seed oil using raw clay as catalyst

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	5013.51	20	250.68	1225.36	< 0.0001	Significant
A-Catalyst conc.	105.59	1	105.59	516.16	< 0.0001	
B-Methanol/oil	130.57	1	130.57	638.28	< 0.0001	
C-Temperature	589.92	1	589.92	2883.66	< 0.0001	
D-Reaction time	1265.22	1	1265.22	6184.71	< 0.0001	
E-Agitation speed	172.80	1	172.80	844.70	< 0.0001	
AB	0.3709	1	0.3709	1.81	0.2052	
AC	5.54	1	5.54	27.06	0.0003	
AD	9.43	1	9.43	46.08	< 0.0001	
AE	1.37	1	1.37	6.69	0.0253	
BC	0.0240	1	0.0240	0.1175	0.7382	
BD	21.01	1	21.01	102.71	< 0.0001	
BE	54.92	1	54.92	268.44	< 0.0001	
CD	382.82	1	382.82	1871.30	< 0.0001	
CE	55.72	1	55.72	272.38	< 0.0001	
DE	30.79	1	30.79	150.51	< 0.0001	
A^2	0.2359	1	0.2359	1.15	0.3059	
B^2	159.38	1	159.38	779.09	< 0.0001	
C^2	99.90	1	99.90	488.33	< 0.0001	
D^2	161.91	1	161.91	791.44	< 0.0001	
E^2	0.0179	1	0.0179	0.0877	0.7727	
Residual	2.25	11	0.2046			
Lack of Fit	0.2503	5	0.0501	0.1502	0.9724	not significant
Pure Error	2.00	6	0.3333			
Cor Total	5015.76	31				

ANOVA was applied to determine significant terms among the independent variables studied. Hence, if the model F-value is significant. The **Model F-value** of 1225.36 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. **P-values** less than 0.0500 indicate model terms are significant. In this case A, B, C, D, E, AC, AD, AE, BD, BE, CD, CE, DE, B^2, C^2, D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. Though model terms highlighted include the single terms, interaction terms and quadratic terms, the terms of interest are the interaction terms. It depicts the interactive relationship between the terms as illustrated by the contour and 3D plots. The **Lack of Fit F-value** of 0.15 implies the Lack of Fit is not significant relative to the pure error. There is a 97.24% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit. All the independent variables studied are represented in the ANOVA table. From the table, reaction time having the highest F-value of 1265.22, has the most significant effect on the response (biodiesel) production. Also, in the same vain, catalyst concentration having the least F-value of 516.16 has the least significant effect. Study on the interaction effects indicates that interaction between temperature and reaction time (CD) having the highest F-value of 1871.30, has the greatest effect, while the interaction between catalyst concentration and temperature (AC) having the least F-value of 27.06 has the least effect.

Table 3b ANOVA table for biodiesel production from orange seed oil using thermal clay as catalyst

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	5299.85	20	264.99	537.91	< 0.0001	significant
A-Catalyst conc.	123.47	1	123.47	250.63	< 0.0001	
B-Methanol/oil	163.49	1	163.49	331.88	< 0.0001	
C-Temperature	551.18	1	551.18	1118.85	< 0.0001	
D-Reaction time	1550.12	1	1550.12	3146.61	< 0.0001	
E-Agitation speed	181.38	1	181.38	368.18	< 0.0001	
AB	5.92	1	5.92	12.02	0.0053	
AC	4.45	1	4.45	9.03	0.0120	
AD	3.91	1	3.91	7.95	0.0167	
AE	2.14	1	2.14	4.35	0.0612	
BC	0.3558	1	0.3558	0.7223	0.4135	
BD	13.76	1	13.76	27.94	0.0003	
BE	43.96	1	43.96	89.23	< 0.0001	
CD	412.31	1	412.31	836.96	< 0.0001	
CE	97.90	1	97.90	198.72	< 0.0001	
DE	56.45	1	56.45	114.58	< 0.0001	
A^2	15.20	1	15.20	30.86	0.0002	
B^2	108.14	1	108.14	219.51	< 0.0001	
C^2	175.41	1	175.41	356.07	< 0.0001	
D^2	77.43	1	77.43	157.17	< 0.0001	
E^2	1.64	1	1.64	3.34	0.0950	
Residual	5.42	11	0.4926			
Lack of Fit	0.9189	5	0.1838	0.2450	0.9279	not significant
Pure Error	4.50	6	0.7500			
Cor Total	5305.27	31				

Table 4 Coefficients of P-Value Shading Using (a) Raw Clay (b) Thermal Modified Clay; as Catalyst in the range $p < 0.05$ $0.05 \le p < 0.1$ $p \ge 0.1$

Parameters	Biodiesel yield	p-values
Intercept	71.7637	
A	2.82853	< 0.0001
B	3.0592	< 0.0001
C	5.96716	< 0.0001
D	10.0261	< 0.0001
E	3.39565	< 0.0001
AB	-0.840232	0.0053
AC	-0.679962	0.0120
AD	0.708208	0.0167
AE	0.494858	0.0612
BC	-0.191762	0.4135
BD	1.10823	0.0003
BE	2.18793	< 0.0001
CD	6.58134	< 0.0001
CE	3.21729	< 0.0001
DE	-2.62417	< 0.0001
A^2	1.85234	0.0002
B^2	-4.65163	< 0.0001
C^2	-6.41388	< 0.0001
D^2	-4.16808	< 0.0001
E^2	-0.53975	0.0950

a

	Biodiesel yield	p-values
intercept	71.7637	
A	2.82853	< 0.0001
B	3.05929	< 0.0001
C	5.96716	< 0.0001
D	10.0261	< 0.0001
E	3.39565	< 0.0001
AB	- 0.840232	0.0053
AC	- 0.679962	0.0120
AD	0.708208	0.0167
AE	0.494858	0.0612
BC	- 0.191762	0.4135
BD	1.10823	0.0003
BE	2.18793	< 0.0001
CD	6.58134	< 0.0001
CE	3.21729	< 0.0001
DE	-2.62417	< 0.0001
A^2	1.85234	< 0.0002
B^2	- 4.65163	< 0.0001
C^2	-6.41388	< 0.0001
D^2	-4.16808	< 0.0001
E^2	-0.53975	0.0905

b

The interactions effects between AC, AD and BC was significant with $p < 0.05$. The quadratic effect of A, B, C, D and E was significant with $p < 0.0001$

Table 5 Fit Statistics using (a) raw clay and (b) thermal clay; as catalyst

Parameters	Values
Std. Dev.	0.4523
Mean	53.09
C.V. %	1.11
R^2	0.8520
Adjusted R^2	0.9987
Predicted R^2	0.9968
Adeq. Precision	130.4329

a

Parameters	Values
Std. Dev.	0.7019
Mean	63.47
C.V. %	1.11
R^2	0.9990
Adjusted R^2	0.9971
Predicted R^2	0.9872
Adeq. Precision	88.9108

b

From the fit statistics table, the **predicted R^2** of 0.9968 is in reasonable agreement with the **adjusted R^2** of 0.9987, the difference being less than 0.2. **Adequacy precision** measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 130.433 indicates an adequate signal. Hence this model can be used to navigate the design space.

Table 6a Coefficients in Terms of Coded Factors using raw clay as catalyst

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	62.84	1	0.2310	62.34	63.35	
A-Catalyst conc.	2.62	1	0.1151	2.36	2.87	1.29
B-Methanol/oil	2.73	1	0.1082	2.50	2.97	1.15

C-Temperature	6.17	1	0.1150	5.92	6.43	1.19
D-Reaction time	9.06	1	0.1152	8.80	9.31	1.25
E-Agitation speed	3.31	1	0.1140	3.06	3.57	1.27
AB	-0.2103	1	0.1562	-0.5540	0.1334	1.46
AC	-0.7587	1	0.1458	-1.08	-0.4377	1.28
AD	-1.10	1	0.1619	-1.46	-0.7427	1.61
AE	0.3955	1	0.1529	0.0589	0.7321	1.55
BC	-0.0498	1	0.1454	-0.3699	0.2702	1.33
BD	1.37	1	0.1351	1.07	1.67	1.24
BE	2.45	1	0.1493	2.12	2.77	1.44
CD	6.34	1	0.1466	6.02	6.66	1.31
CE	2.43	1	0.1471	2.10	2.75	1.27
DE	-1.94	1	0.1580	-2.29	-1.59	1.46
A^2	0.2307	1	0.2149	-0.2422	0.7036	1.35
B^2	-5.65	1	0.2023	-6.09	-5.20	1.30
C^2	-4.84	1	0.2190	-5.32	-4.36	1.39
D^2	-6.03	1	0.2142	-6.50	-5.56	1.51
E^2	0.0564	1	0.1904	-0.3628	0.4755	1.20

Table 6b Coefficients in Terms of Coded Factors using thermal clay as catalyst

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	71.76	1	0.3584	70.97	72.55	
A-Catalyst conc.	2.83	1	0.1787	2.44	3.22	1.29
B-Methanol/oil	3.06	1	0.1679	2.69	3.43	1.15
C-Temperature	5.97	1	0.1784	5.57	6.36	1.19
D-Reaction time	10.03	1	0.1787	9.63	10.42	1.25
E-Agitation speed	3.40	1	0.1770	3.01	3.79	1.27
AB	-0.8402	1	0.2423	-1.37	-0.3069	1.46
AC	-0.6800	1	0.2263	-1.18	-0.1818	1.28
AD	0.7082	1	0.2512	0.1552	1.26	1.61
AE	0.4949	1	0.2373	-0.0275	1.02	1.55
BC	-0.1918	1	0.2256	-0.6884	0.3049	1.33
BD	1.11	1	0.2097	0.6467	1.57	1.24
BE	2.19	1	0.2316	1.68	2.70	1.44
CD	6.58	1	0.2275	6.08	7.08	1.31
CE	3.22	1	0.2282	2.71	3.72	1.27
DE	-2.62	1	0.2451	-3.16	-2.08	1.46

A^2	1.85	1	0.3334	1.12	2.59	1.35
B^2	-4.65	1	0.3140	-5.34	-3.96	1.30
C^2	-6.41	1	0.3399	-7.16	-5.67	1.39
D^2	-4.17	1	0.3325	-4.90	-3.44	1.51
E^2	-0.5398	1	0.2955	-1.19	0.1107	1.20

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 multi-colinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable.

Final Equation in Terms of Coded Factors using raw clay as catalyst

$$Y = +62.84 +2.62A +2.73B +6.17C +9.06D +3.31E -0.2103AB -0.7587AC -1.10AD +0.3955AE -0.0498BC +1.37BD +2.45BE +6.34CD +2.43CE -1.94DE +0.2307A^2 -5.65B^2 -4.84C^2 -6.03D^2 +0.0564E^2$$

Final Equation in Terms of Coded Factors using thermal clay as catalyst

$$Y = +71.76 + 2.83A + 3.06B + 5.97C + 10.03D + 3.40E - 0.8402AB - 0.6800AC + 0.7082AD + 0.4949AE - 0.1918BC + 1.11BD + 2.19BE + 6.58CD + 3.22CE - 2.62DE + 1.85A^2 - 4.65B^2 - 6.41C^2 - 4.17D^2 - 0.5398E^2$$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

3.2. Effects of Catalyst concentration, Temperature, Reaction Time and Agitation speed on the biodiesel yield

Figure 1-3 shows the effect of catalyst concentration as it interacts with other variables on the biodiesel yield. The figures showed that maximum biodiesel was achieved at a time of 150 minutes, temperature of 65 °C, and agitation speed of 250 rpm.

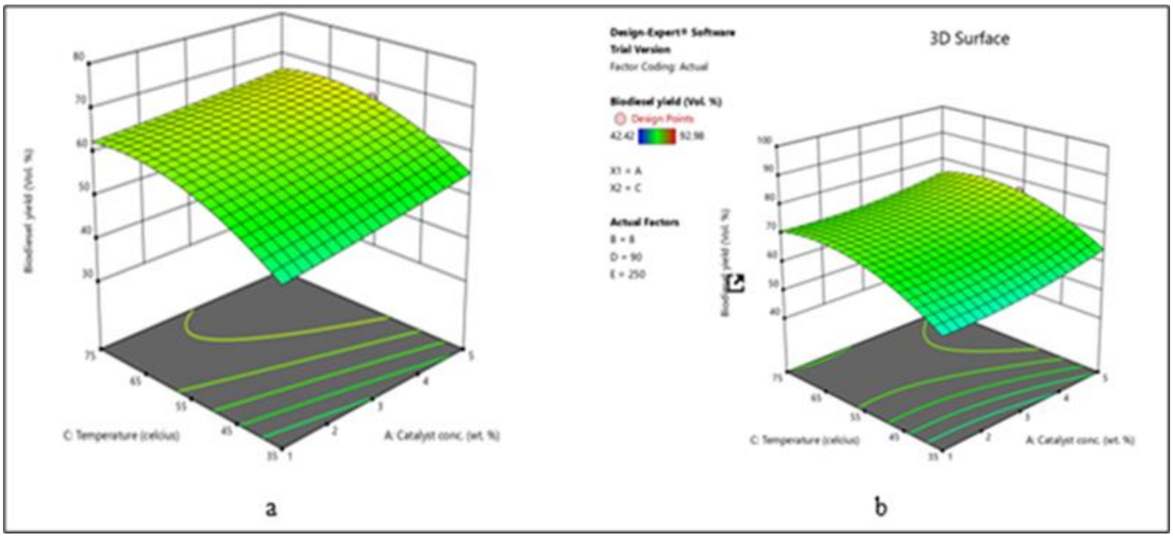

Figure 1 (a) Effect of Catalyst concentration (wt. %) and Temperature (°C) using raw clay as catalyst; (b) Effect of Catalyst concentration (wt. %) and Temperature (°C) using thermal clay as catalyst

The combined effect of catalyst concentration and temperature on the biodiesel produced from the orange seed oil at methanol/oil mole ratio 12:1 (w/w) and catalyst loading 4% wt is shown in figure 1. This showed an increase in the biodiesel yield when the temperature was 65 °C.

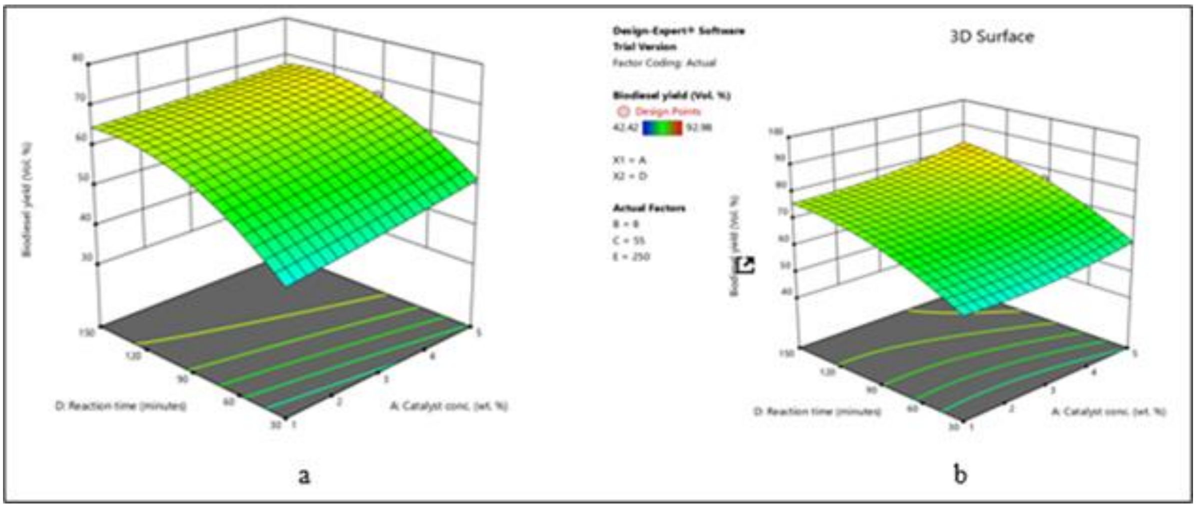

Figure 2 (a) Effect of Catalyst concentration (wt. %) and Reaction time (minutes) using raw clay as catalyst; (b) Effect of Catalyst concentration (wt. %) and Reaction time (minutes) using thermal clay as catalyst

The combined effect of catalyst concentration and reaction time on the biodiesel produced from the orange seed oil at methanol/oil mole ratio 12:1 (w/w) and catalyst loading 4% wt is shown in figure 2. This showed an increase in the biodiesel yield when the reaction time was 120 minutes.

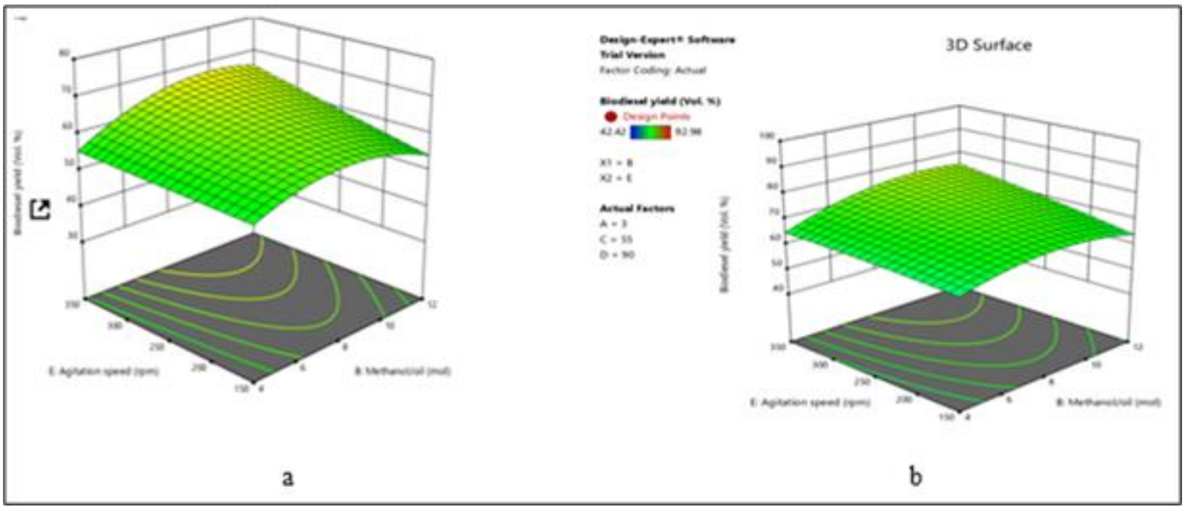

Figure 3 (a) Effect of Catalyst concentration (wt. %) and Agitation speed (rpm) using raw clay as catalyst; (b) Effect of Catalyst concentration (wt. %) and Agitation speed (rpm) using thermal clay as catalyst

The combined effect of catalyst concentration and agitation speed on the biodiesel produced from the orange seed oil at methanol/oil mole ratio 12:1 (w/w) and catalyst loading 4% wt is shown in figure 3. This showed an increase in the biodiesel yield with increase in agitation speed.

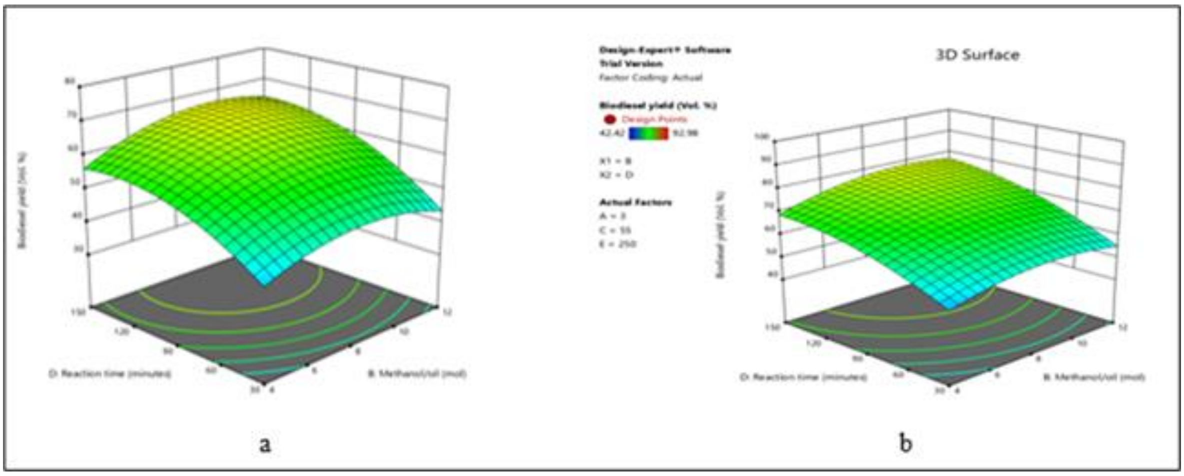

Figure 4 (a) Effect of Methanol/Oil ratio (mol) and Reaction time (minutes) using raw clay as catalyst; (b) Effect of Methanol/Oil ratio (mol) and Reaction time (minutes) using thermal clay as catalyst

The combined effect of methanol/oil ratio and reaction time on the biodiesel produced from the orange seed oil at methanol/oil mole ratio 12:1 (w/w) and catalyst loading 4% wt is shown in figure 4. This showed an increase in the biodiesel yield at a reaction time of 90 minutes and showed a decrease when the time was further increased.

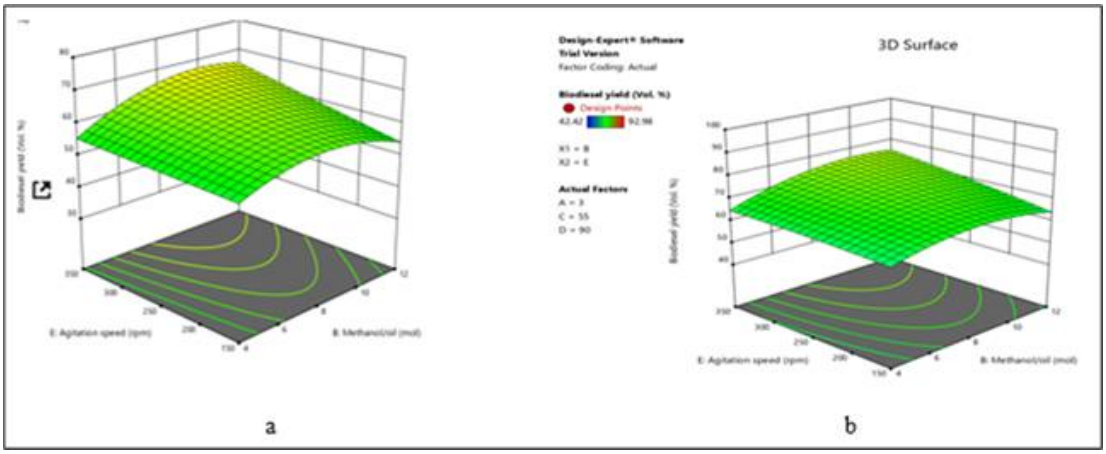

Figure 5 (a) Effect of Methanol/Oil ratio (mol) and Agitation sped (rpm) using raw clay as catalyst; (b) Effect of Methanol/Oil ratio (mol) and Agitation sped (rpm) using thermal clay as catalyst

The combined effect of methanol/oil ratio and agitation speed on the biodiesel produced from the orange seed oil at methanol/oil mole ratio 12:1 (w/w) and catalyst loading 4% wt is shown in figure 5. This showed an increase of 67.5 % in the biodiesel yield at an agitation speed of 250 rpm and a further increase in agitation speed caused a decrease in the biodiesel yield.

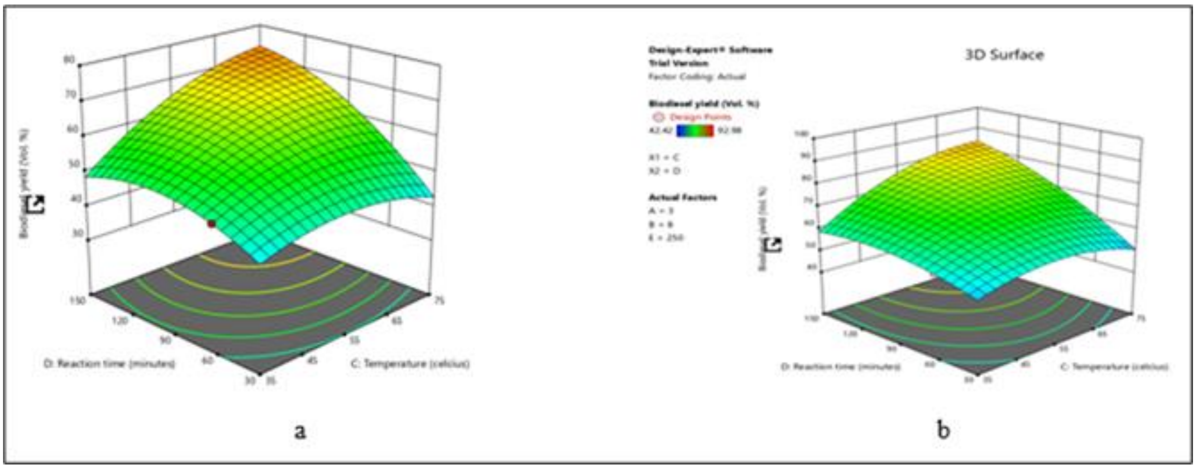

Figure 6 (a) Effect of Temperature (°C) and Reaction Time (minutes) using raw clay as catalyst; (b) Effect of Temperature (°C) and Reaction Time (minutes) using thermal clay as catalyst

The combined effect of temperature and reaction time on the biodiesel produced from the orange seed oil at methanol/oil mole ratio 12:1 (w/w) and catalyst loading 4% wt is shown in figure 6. It showed an increase in the biodiesel yield when the temperature was 75 °C and reaction time of 150 minutes.

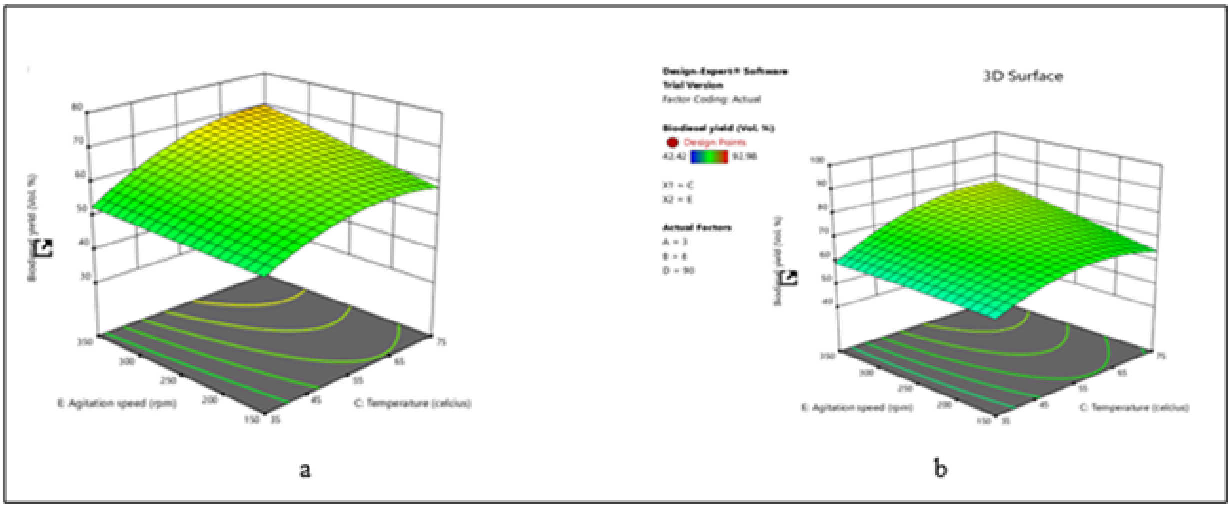

Figure 7 (a) Effect of Temperature (^{0}C) and Agitation Speed (rpm) using raw clay as catalyst; (b) Effect of Temperature (^{0}C) and Agitation Speed (rpm) using thermal clay as catalyst

The combined effect of temperature and agitation speed on the biodiesel produced from the orange seed oil at methanol/oil mole ratio 12:1 (w/w) and catalyst loading 4% wt is shown in figure 7. At a low temperature of 35 °C and agitation speed of 150 rpm, the biodiesel yield was 53.50%, but when the agitation speed was increased to75 rpm at a temperature of 350 ^{0}C, the biodiesel yield increased to 70.08%.

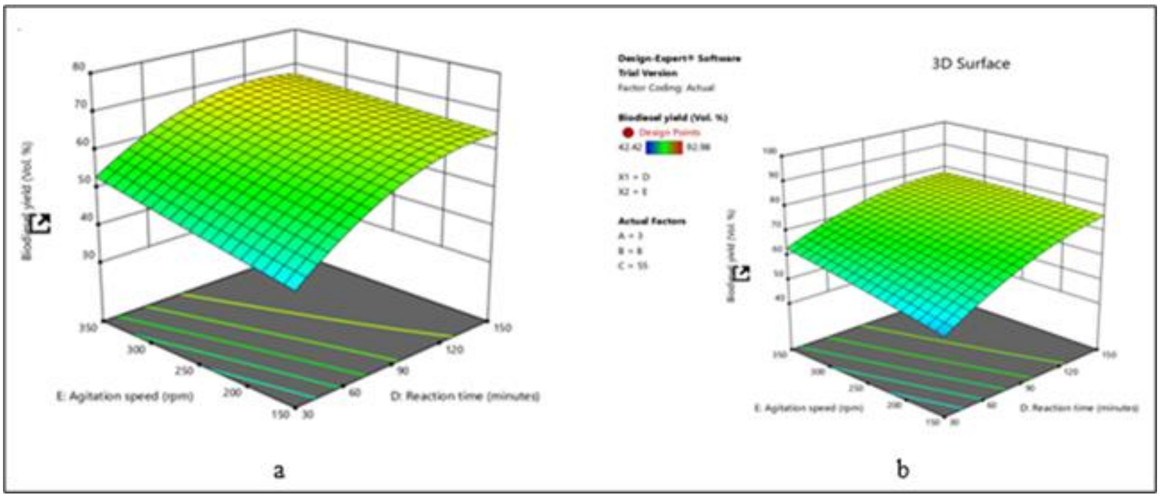

Figure 8 (a) Effect of Reaction Time (minutes) and Agitation speed (rpm) using raw clay as catalyst; (b) Effect of Reaction Time (minutes) and Agitation speed (rpm) using thermal clay as catalyst

The combined effect of reaction time and agitation speed on the biodiesel produced from the orange seed oil at methanol/oil mole ratio 12:1 (w/w) and catalyst loading 4% wt is shown in figure 8. This showed an increase in the biodiesel yield of about 68% when the agitation speed was 250 rpm and reaction time of 120 minutes and showed a decrease when the reaction time and the agitation speed was further increased.

4. Conclusion

With the recent decline in the oil industry and a search for a cleaner environment and a safer energy, it can be concluded that orange seed oil can be applied for biodiesel production. Also heterogeneous catalyst as such from clay composing of kaolinite, can be used to speed up the reaction. The raw clay catalyst produced varied effect on the biodiesel yield. From the matrix design, set of optimal condition for biodiesel production is; catalyst concentration 3wt %, methanol to sample ratio in mole 12:1, Temperature 65 °C, reaction time 150 minutes and agitation speed 300 rpm. Analysis using central composite design suggests that all the process parameters had significant effect on biodiesel yield. There is also the reaffirmation of cleaner energy as CO_2 and CO emitted by biodiesel during fuel combustion test was less than the quantity emitted by petrol diesel.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

References

[1] Agbede, O. O. (2012). Evaluation of Chosen Fruit Seed Oils as Potential Biofuel. Journal International Agrophysics, 26(2): 199-202.

[2] Ajala, E. O., Aberuagba, F., Olaniyan, A. M., Ajala, M. A. and Sunmonu, M. O. (2017). Optimization of A Two Stage Process For Biodiesel Production From Shea Butter Using Response Surface Tehnology. Egyptian Journal of Petroleum, 26: 943-955.

[3] Banerjee, N., Ramakrishnan, R. and Jash, T. (2014). Biodiesel Production From Used Vegetable Oil Collected From Shop Selling Fritters In Kolkata. Energy Procedia, 54:161-165.

[4] Bull, O. S. and Obunwo, C. C. (2014). Biodiesel Production from Orange (Citrus Sinesis) Peels as Feedstock. Journal of Applied Science Environmental Management, 18(3): 371-374.

[5] Heydarzadeh, J. K., Marzban, N., Najafpour, G. D. and Valizadeh, S. (2018). Development of A Nano Alumina – Zirconia Composite Catalyst As An Active Thin Film In Biodiesel Production. Indian Journal of Chemical Technology, 25(6): 578-582.

[6] Ibifubara, H., Obot, N.I. and M.A. Chendo (2014). Utilization of Some Non-Edible Oil for Biodiesel Production. Nigeria Journal of Pure and Applied Physics, 7(1): 10-20.

[7] Mishra, R. S., Amit .P. and Anand, P. M. (2015). Effects of Homogeneous catalysts on Production of Biodiesel from Crude Neem Oil Feed stock and Cost Analysis of Biodiesel Production. International Journal of Advance Research and Innovation, 3(3): 503-507.

[8] Montefri, M.J. and Obbard, J.P (2010). The Economic of Biodiesel Derived from Waste Cooking Oil in the Philippines. Energy Sources, Part B. Economic, Planning and Policy. 5(4): 337-347.

[9] Onukwuli, O. D., Emembolu, L., Nonso, C., Aliozo, S. O. and Menkti, M. C. (2016). Optimization of Biodiesel Production from Refined Cotton Seed Oil and its Characterization. Egyptian Journal of Petroleum, 26(1).

[10] Savariraj, S., Ganapathy, T. and Saravanam, C. G. (2011). Experimental Investigation of Performance and Emission Characteristics of Mahua Biodiesel in Diesel Engine. Renewable Energy, 20(11):1-6.

[11] Sirajudin, N., Jusoff, K., Yani, Setyawali, Ifa, L. and Rossyadi, A. (2013). Biofuel Production from Catalytic Cracking of Palm Oil. Bulletin of Chemical Reaction Engineering and Catalysts, 7(3):185-190.

[12] Yousef, M., Natheghi, L. and Gholamian, M. (2013). Physiochemical Properties of Two Types of Shahrodi Grape Seed Oil (Lai and Khalili). European Journal of Experimental Biology, 3(5):115-118.

[13] Victor Dominic Teku, (2017). Modified Kaolinite Clay as Catalysts for Biodiesel Production from Waste Cooking Oil, PhD Thesis, Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria.

[14] Zhang, Y., Dube, M. A., and Mclean D. D. (2003). Biodiesel Production from Waste Cooking Oil: 1. Process Design and Technology Assessment. Bioresource Technology, 90: 229-240

[15] Zullaikah, C. L., Vali, S. R. and Yi-Hsu S. (2005). A Two-Step Acid-Catalyzed Process for The Production of Biodiesel From Rice Bran Oil. Bioresource Technology, 96(17):1889-1896.