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Application of Response Surface Design for the Optimization of Biodiesel Production from Desert Date (*Balanite aegyptiaca*) Oil

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Abstract: Biodiesel is another form of renewable energy with various applications. In this context, biodiesel characterization showed that kinematic viscosity at 40°C was 5.3, cetane number was 68.1, flash point 240, pour point was -12, density was 0.85, specific gravity was 0.85, sulfated ash was 0.6, copper strip corrosion test was 1b and the high heating value was 42.4. The empirical model obtained showed that reaction time, catalyst concentration and reaction temperature are the most important variables that influence the process. Irrespective of the amount of methanol employed, biodiesel yields in excess of 69% were obtained only when the trans-esterification taken place at temperature of 65°C for 74 mins. The optimal process condition was discovered to be when the temperature, reaction time and catalyst concentration were 66.26°C, 74.4 minutes and 5.23 M, respectively. Validation results (68.7 ± 0.8%) are generally in agreement with the predicted value of 70.04%.

Keywords: Biodiesel, Triglyceride, Box-behnken, Response Surface, Transesterification

1. Introduction

The availability of energy in an area determines the socio-economic development of such an area. While the socio-economic development of a nation depends largely on the availability and the consumption of energy, the quest to find an alternative source of energy to replace the fast depleting fossil fuel becomes necessary. Thus, this prompted the attempt and use of biodiesel as an energy supply technology.

Recently, energy need is increasing tremendously in most of the developing countries and continuous increment in crude oil price is becoming unbearable and this was aggravated due to the remediation of environmental pollution surfaced during processing, dwindling of production charge [1]. This, inevitably, shows an unfavorably influence on the economy of both oil importing and exporting countries [2]. Therefore, the afore-mentioned obsessive issues were observed and initiate more ideas on providing alternative source of energy [3].

Biodiesel is a new alternative source of fuel that produced from renewable resources or agricultural wastes that can be replenish in a short period of time. Biodiesel does not include petroleum but can be mix with the petroleum diesel to form biodiesel mixture. It is applicable in compression-ignition (CI-diesel) engines with few or no adjustment. It is not complicated to use, decomposable, non-poisonous and most importantly free of sulphur and aromatics [4].

According to [5], B. aegyptiaca is spiny branches, highly drought tolerant evergreen plant, a dicotyledonous flowering species, belongs to Zygophyllaceae family. The tree has bushy, tough leaves, and a double root system, and produces date-like fruits. It is also a thorny species which has 2.5-3.5 cm lengthy thorns. The aim of this research is to study the application of response surface design for the optimization of biodiesel production from desert date (*Balanite aegyptiaca*) oil.

2. Materials and Methods

2.1. Sample Collection and Preparation

The desert date fruits used for this work were obtained from Rafin Bauna in Aliero local government area in Kebbi state of Nigeria. After collection, they were sun dried and their shells cracked using metal hammer to obtain its seed and dried seeds were crushed into cake using mortar to enhance extraction.

2.2. Oil Extraction

About 150 ml of normal hexane was poured into round bottom flask. 100 g of the sample was placed in the thimble and was inserted in the centre of the extractor. The Soxhlet was heated at 65°C. When the solvent is boiling, the vapour rises through the vertical tube into the condenser at the top. The liquid condensate drips into the thimble in the centre, which contains the solid sample to be extracted. The extract seeps through the pores of the thimble and fills the siphon tube, where it flows down ward into the round bottom flask and was continued for a period of 4-6 hours [6]. It was then removed from the tube, dried in the oven, cooled in the desiccators and weighed again to determine the amount of oil extracted. Further extraction was carried out. The extracted oil was stored in a container for subsequent characterization.

2.3. Experimental Design

Response surface (Box-Behnken) statistical design was used for the optimization experiments. Independent parameters such as reaction time, temperature, amount of methanol and catalyst (cement clinker) concentration were selected for the investigation based on preliminary experiments conducted. Each run was set in duplicate and all the runs were completely randomized to obtain a total of 54 runs. The experiment was designed using MINITAB 16 Statistical Software and the data that was collected from the experiments was analyzed using same software at a D 0.05 (95% confidence level).

2.4. Transesterification Process

Trans-esterification was taken place at different time range of 30 mins to 120 mins, various temperature ranged from 40°C to 80°C, various methanol volume ranged from 2.2 mL to 4.4 mL, various catalyst concentration ranged from 0.2g to 1.0g at different run order with the help of stirring. Water was used to remove the glycerol and water soluble methanol by washing and the biodiesel undergo filtration in order to remove the residual methanol and catalyst before evaporation taking place [7].

The biodiesel thus obtained was further analyzed to investigate its properties so as to be sure that the produced material would be able to serve its purpose.

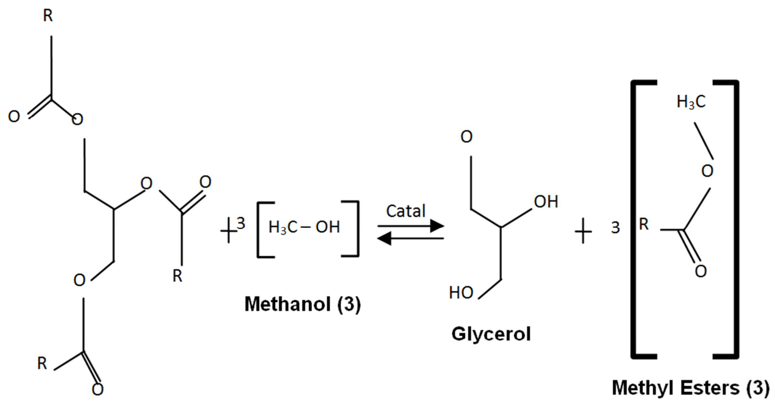

Figure 1. *Trans-esterification reaction.*

2.5. Determination of Biodiesel Fuel Properties

2.5.1. Kinematic Viscosity (ASTM D 445-06)

A viscometer is inserted into a water bath with a set temperature and left for 30minutes. The sample is added to the viscometer and allowed to remain in the bath as long as it reaches the test thermometer. The sample is allowed to flow freely and the time required for the meniscus to pass from the first to the second timing mark is taken using a stop watch. The procedure is repeated a number of times and the average value are taken which is then multiplied with the viscometer calibration to give the kinematic viscosity [8].

2.5.2. Flash Point (ASTM D 93-08)

A sample of the biodiesel is heated in a close vessel and ignited. When the sample burns, the temperature was recorded, the pensky-martens cup tester measures the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. The biodiesel is placed in a cup in such quantity as to just touch the prescribed mark on the interior of the cup. The cover is then fitted onto the position on the cup and Bunsen burner is used to supply heat to the apparatus at a rate of about 5°C per minute. During heating, the oil is constantly stirred. As the oil approaches its flashing, the injector burner is lighted and injected into the oil container after every 12 second intervals until a distinct flash is observed within the container. The temperature at which the flash occurred is then recorded, it is repeated three times and the average taken [9].

2.5.3. Pour Point (ASTM D 97-11)

The sample was kept in the freezer to about 50°C and then placed in a heating mantle to melt. The temperature at the bottom of the test jar that is the temperature at which the biodiesel starts to pour is taken as the pour point [10].

2.5.4. Cetane Number (ASTM D 613-17b)

Cetane Number is the determination of delay in an ignition of fuel. Increase in cetane numbers shows shorter ignition time. Increase in cetane numbers reduced engine roughness and with lower starting temperature for engine [10].

2.5.5. Sulfated Ash (ASTM D874)

This is used to determine the proportion of non-volatilized substances in the sample when the sample is ignited in the presence of sulphuric acid. It is also used to determine the presence of inorganic impurities in an organic substance [11].

2.5.6. Density (ASTM D1298-99)

The weight of an empty 25ml measuring cylinder was taken as Mo and later filled up with biodiesel to be indicated as MV. Hence, the density was evaluated using the equation below [12].

$$\mathrm{Density} = \mathrm{Mo} - \mathrm{MV}$$

2.5.7. Specific Gravity (ASTM D1298-99)

It can be determined by the equation below [12].

$$\mathrm{SG} = \mathrm{DensityoftheobjectDensityofwater}$$

2.5.8. Copper Strip Corrosion Test (ASTM D130)

Polished copper strip was suspended into the product and its effect observed and classified ranging from 1 – 4 on the ASTM copper strip corrosion standard [13].

2.5.9. High Heating Value (HHV) (ASTM D6751)

High heating value also known as gross calorific value is the specific quantity of heat released during the burning of a certain amount of fuel sample. It is calculated using the equation below [14].

3. Results

Table 1. *Results of analysis of variance for desert date biodiesel yield (%).*

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	6	1365.39	227.566	4.42	0.001
Linear	3	456.38	152.126	2.96	0.042
Square	3	909.02	303.005	5.89	0.002
Error	47	2417.88	51.444		
Lack-of-Fit	18	1895.29	105.294	5.84	0.000
Pure Error	29	522.59	18.020		
Total	53	3783.28			

DF = degree of freedom, Adj SS = adjusted sums of squares, Adj MS=adjusted mean squares, F = F – statistic, and P = p – value using p value of 0.05 at 90% confidence limit.

Table 2. *Results of regression analysis.*

Term	Effect	Coef	SE Coef	T-Value	P-Value	VIF	Significance
Constant		68.74	2.18	31.50	0.000		
CatCon (c)	-4.69	-2.34	1.46	-1.60	0.116	1.00	ns
Temp (d)	7.35	3.67	1.46	2.51	0.016	1.00	s
Time (t)	-0.34	-0.17	1.46	-0.12	0.907	1.00	ns
CatCon *CatCon (c^2)	-11.96	-5.98	2.07	-2.89	0.006	1.11	s
Temp *Temp (d^2)	-11.92	-5.96	2.07	-2.88	0.006	1.11	s
Time *Time (t^2)	-12.98	-6.49	2.18	-3.11	0.003	1.11	s

s =statistically significant, and ns = statistically not significant Coef = regression equation coefficients, SE Coef = Standard error for coefficients, T = t – statistic, P = p – value.

Regression Equation in Uncoded Units

$$\mathrm{Yield\ (\%)} = -23.6 + 3.90\,(\mathrm{c}) + 1.972\,(\mathrm{d}) + 0.477\,(\mathrm{t}) - 0.374\,(\mathrm{c_2}) - 0.01490\,(\mathrm{d_2}) - 0.00321\,(\mathrm{t_2})$$

Fits and Diagnostics for Unusual Observations

Obs	Yield (%)	Fit	Resid	Std	Resid
1	53.55	68.74	-15.19	-2.22	R
31	53.25	68.74	-15.49	-2.27	R

R: Large residual.

Table 3. *Results of Optimization.*

Parameters						
Response	**Goal**	**Lower**	**Target**	**Upper**	**Weight**	**Importance**
Yield (%)	Maximum	42.027	76.043		1	1

Solution	**Cat Con (%)**	**Temp (°C)**	**Time (min)**	**Yield (%)**	**Desirability**
Local solution 1	5.23232	66.2626	74.4004	69.5368	0.808730
Local solution 2	4.31688	70.0693	64.7063	68.7054	0.784291
Local solution 3	4.29465	70.1646	84.7085	68.6406	0.782383
Local solution 4	6.82482	70.8493	61.9803	67.7474	0.756127
Global solution	6.84417	70.9051	87.3656	67.6729	0.753936

Multiple Response Prediction	
Variable	**Setting**
CatCon (%)	5.23232
Temp (°C)	66.2626
Time (min)	74.4004

Response	**Fit**	**SE Fit**	**95% CI**	**95% PI**
Yield (%)	69.54	2.08	(65.35, 73.73)	(54.51, 84.56)

Table 4. *Fuel characterization of the biodiesel.*

Parameter	**Value**	**ASTM**
Kinematic viscosity cSt at 40°C	5.3	1.9–6.0 ASTM D 445-06
Cetane number	68.1	47–65 ASTM D613-17b
Flash point (°C)	240	>130 ASTM D 93-08
Pour point (°C)	-12	(-15) -10 ASTM D 97-11
Density (g/cm^3)	0.85	0.845 ASTM D 1298-99
Specific gravity	0.85	0.88 ASTM D 1298-99
Sulphated ash (%)	0.6	0.02 ASTM D 874-08b
Copper strip corrosion test	1b	1 – 3max ASTM D 130-08
High heating value (MJ/Kg)	42.4	43 ASTM D 6751-08

Contour plots

Figures 1-3 are contour plots describing the relationship between any two of the process variables as they affect the biodiesel yield while holding the other two variables constant.

Table 5. *Result for transesterification.*

RunOrder	**CatCon (g)**	**MeOH (cm^3)**	**Temp (C)**	**Time (min)**	**Yield (g)**	**Yield (%)**
1	0.60	3.3	60	75	5.3554	53.55
2	0.20	3.3	80	75	5.6259	56.26
3	0.20	3.3	40	75	4.7023	47.02
4	1.00	3.3	60	30	4.4002	44.00
5	0.60	3.3	40	120	4.2027	42.03
6	0.60	4.4	60	120	5.7975	57.98
7	0.60	4.4	40	75	6.5781	65.78
8	0.60	4.4	60	120	5.7791	57.79
9	0.60	3.3	80	30	6.5968	65.97
10	0.20	3.3	60	120	6.9124	69.12
11	0.20	4.4	60	75	6.8785	68.79
12	0.60	2.2	40	75	7.2435	72.44
13	0.60	3.3	80	120	5.7969	57.97
14	0.60	3.3	40	120	4.2232	42.23
15	1.00	3.3	40	75	5.2363	52.36
16	0.60	2.2	60	120	5.9595	59.60
17	1.00	4.4	60	75	5.6743	56.74
18	0.60	3.3	40	30	4.9367	49.37
19	1.00	2.2	60	75	5.7969	57.97

RunOrder	CatCon (g)	MeOH (cm^3)	Temp (C)	Time (min)	Yield (g)	Yield (%)
20	0.60	3.3	40	30	4.9888	49.89
21	1.00	4.4	60	75	5.6634	56.63
22	1.00	3.3	60	120	6.2083	62.08
23	0.60	4.4	40	75	6.586	65.86
24	1.00	3.3	40	75	5.3024	53.02
25	0.20	3.3	40	75	4.1002	47.00
26	0.60	2.2	80	75	6.4221	64.22
27	0.60	4.4	80	75	6.7167	67.17
28	0.60	2.2	60	30	6.4137	64.14
29	1.00	3.3	80	75	6.3019	63.02
30	0.20	3.3	60	30	5.8356	58.36
31	0.60	3.3	60	75	5.3246	53.25
32	0.20	2.2	60	75	6.6589	66.59
33	0.60	2.2	60	30	6.3566	63.57
34	1.00	3.3	80	75	6.3516	63.52
35	0.20	4.4	60	75	6.8654	68.65
36	1.00	2.2	60	75	5.8563	58.56
37	0.20	3.3	80	75	5.5508	55.51
38	1.00	3.3	60	30	4.4448	44.45
39	0.20	3.3	60	30	5.8497	58.50
40	0.60	2.2	60	120	5.9726	59.73
41	0.60	2.2	80	75	6.4384	64.38
42	0.60	3.3	60	75	7.6014	76.01
43	0.60	3.3	80	30	6.5234	65.23
44	0.60	4.4	60	30	6.9024	69.02
45	1.00	3.3	60	120	6.2798	62.80
46	0.20	2.2	60	75	6.6593	66.59
47	0.60	3.3	80	120	5.682	56.82
48	0.60	3.3	60	75	7.6043	76.04
49	0.60	3.3	60	75	6.7147	67.15
50	0.60	4.4	60	30	6.8789	68.79
51	0.60	3.3	60	75	6.7163	67.16
52	0.60	2.2	40	75	7.2389	72.39
53	0.60	4.4	80	75	6.748	67.48
54	0.20	3.3	60	120	6.9034	69.03

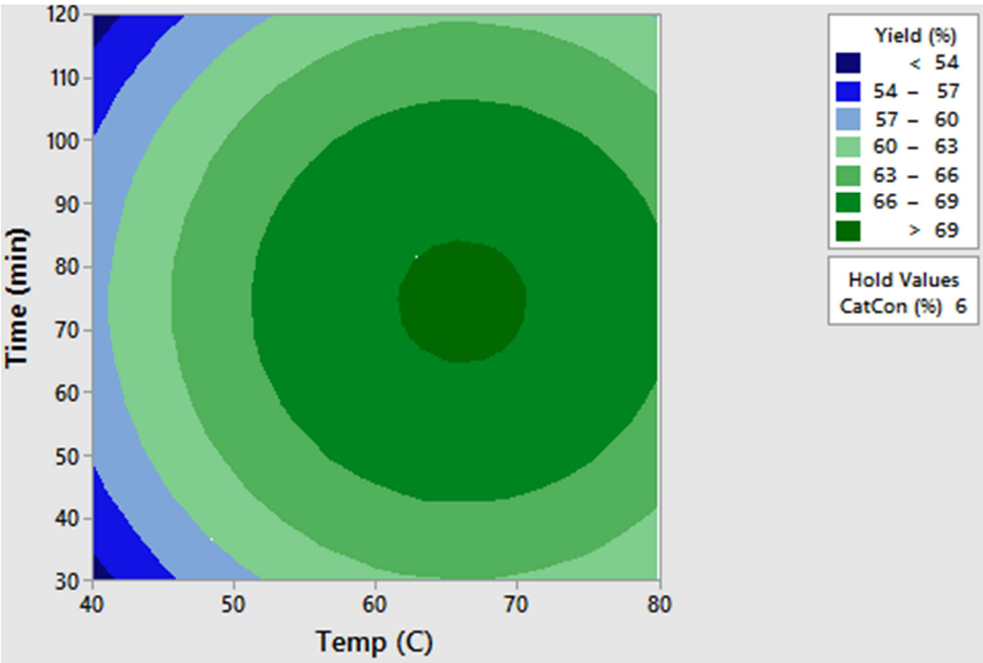

Figure 2. Contour plot showing the relationship between reaction time and temperature on biodiesel yield with the catalyst concentration held constant.

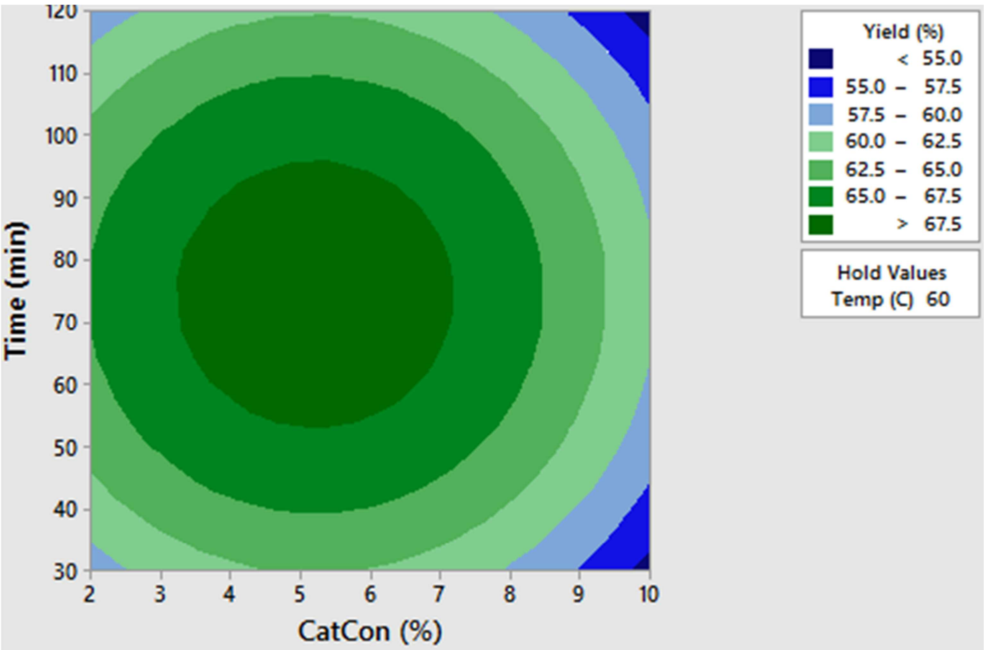

Figure 3. *Contour plot showing the relationship between the reaction time and catalyst on biodiesel yield with the temperature held constant.*

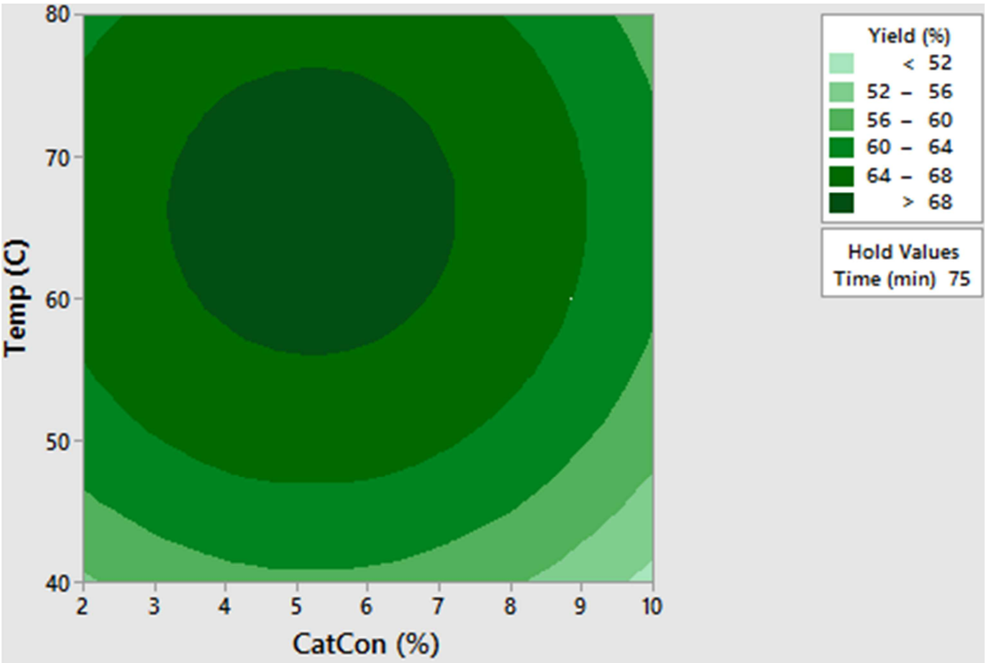

Figure 4. *Contour plot showing the relationship between the temperature and catalyst concentration on biodiesel yield with time held constant.*

4. Discussion

Regression analysis and their significance

Temperature (d) and their respective squares (c^2, d^2 and t^2), all other linear and square terms of the process variables are statistically insignificant ($p > 0.05$). With five (4) significant terms and two insignificant terms show that the basic requirements of the regression analysis have been met.

Optimization and validation of the biodiesel yield

Optimization of the biodiesel yield was carried out using Response Optimizer in Minitab 17 Statistical Software. Table 3 shows the three optimal solutions obtained from the optimization. All the solutions have variable amounts of catalyst concentration, temperature and reaction times Furthermore, there doesn't seem to be much difference amongst the solutions in terms of the temperature. The most significant difference amongst the solutions is the reaction temperature. Solutions 4, with relatively high temperature of about (70.8°C), predicts a relatively low biodiesel yield of about 67.7%. On the other hand, the relatively low temperature (70.1°C) involved in Solution 3 makes it less attractive than Solution 1. Thus, the global solution (Local Solution 1) which requires moderate temperature of about

66°C with predicted biodiesel yield of about 69.5% may therefore be more attractive for the transesterification of desert date seed oil into biodiesel. Biodiesel yield of 68.7 ± 0.8% was obtained from validation experiments conducted at the levels of the process variables predicted in Solution 1.

Although one-sample t-test reveals that the empirical yield is significantly less than the model prediction, the two are quite close with a difference of less than 1%. This further indicates that the empirical model obtained from the response surface design is highly reliable and a very good presentation of the process. It is noteworthy that higher yields can be obtained at long reaction time while holding the temperature and catalyst concentration at 66°C and 5.2%, respectively.

Contour plots description of the relationship between variables

Figures 1-3 are contour plots describing the relationship between any two of the process variables as they affect the biodiesel yield while holding the other one variable constant. The biodiesel yield increased with increasing reaction time and reaction temperature. At a lower reaction time and temperature (< 40 minutes, < 50°C), the biodiesel yield was less than 57.0%. Highest yields, in excess of 70%, were obtained at reaction times > 70 minute when the reaction temperature was > 65°C (Figure 2). Catalyst concentration and reaction time also interact positively to influence the biodiesel yield (Figure 3). When reaction time was below 90 minutes, the biodiesel yield was < 67.5% with respect to the concentration of the catalyst at 5.5%. Maximum yields of biodiesel (> 67.5%) were obtained when the transesterification was conducted for 60 to 70 minutes (Figure 3).

The relationship between the two variables (catalyst and time) on biodiesel yield at 65 minutes and 5.5% catalyst concentration in Figure 3 displayed similar trend as Figure 2. Figure 4 showed that biodiesel yields of over 70% can be obtained when the concentration of the catalyst was between 4.5% and 5.5% while the temperature was above 60°C.

Properties of the biodiesel

The biodiesel produced was characterized using ASTM standard methods as shown in Table 1. Sulfated ash is slightly above the ASTM minimum limit. All other parameters as seen in table 1 are however in agreement with the ASTM standard specifications and values obtained from conversion of desert date seed oil into biodiesel.

5. Conclusion

Response surface methodology was successfully applied for transesterification of methanol. The high regression coefficients of the second-order polynomial showed that the model was well fitted to the experimental data. The ANOVA implied that molar ratio of alcohol to oil; reaction temperature and concentration of catalyst have the great significant factor affecting the yield of biodiesel. The optimal process condition was discovered to be when the temperature, reaction time and catalyst concentration were 66.26°C, 74.4 minutes and 5.23 M, respectively.

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