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Optimization of biodiesel production from castor oil by response surface methodology

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Abstract

This work investigated the possibility of using response surface methodology based on a four factor five level central composite design to optimize biodiesel production from castor oil. The reaction variables were oil: ethanol ratio, lipozyme concentration, time and temperature. The properties of the biodiesel produced were assessed. The linear coefficient of lipozyme concentration (B), temperature (D), the quadratic coefficient of lipozyme concentration (B^2), time (C^2), temperature (D^2), the interaction of oil/ethanol ratio and lipozyme concentration (A*B), the interaction of lipozyme concentration and time (B*C) had significant effect on the biodiesel yield ($p<0.05$).The other variableswere not significant ($p>0.05$).The specific gravity was (0.91), refractive index (1.41 ± 0.01), viscosity (14.1), cetane number (53.9), calorific value (38.0± 0.10), flash point (150°C), cloud point (7°C) iodine value (101 ± 0.53), acid value (0.57 ± 0.01), and saponification value (180±0.25). Maximum yield was found to be 93.0% under the conditions of oil: ethanol ratio of (1:7.14), lipozyme concentration (40 U), time (165 min) and temperature 50°C.The properties of the biodiesel produced were largely in conformity with ASTM D6751 standards.

Keywords: Biodiesel, castor oil, optimization, transesterification

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Introduction

The rapid depletion of world's petroleum reserves and increased ecological concerns have prompted the demand of environment friendly renewable energy resources (Ashish et al., 2010). The development of alternative energy source to extend the fossil fuels has received a large interest in the last few decades due to an increasing concern to protect the environment and conserve the nonrenewable natural energy resources (Vicente et al., 1998).

A number of processes such as chemical, enzymatic and supercritical alcohol treatment have been employed for biodiesel production (Warabi et al., 2004). Transesterification reaction consists of reversible reactions between alcohol and triacylglycerol present in oil or fats to produce three moles of fatty acid alkyl esters and glycerol as a co-product (Abdullahi et al., 2009). The use of non-edible oils such as karanja, polanga, jatropha, and castor oil have attracted great attention as they do not pose threats to food security when used as feedstock in fuel industry (Koh and Mohd, 2011).

Several parameters, such as the type of catalyst, alcohol/ oil molar ratio, temperature, purity of the reactants and free fatty acid content have a greater influence on the transesterification reaction (Giovanilton et al., 2011).

This study's main objective was to develop an approach for better understanding the relationships between the variables (factors) and the response ethyl ester formation to obtain the optimum conditionsthat will improve the biodiesel yieldusing response surface methodology (RSM).

Materials and methods

Collection of castor seed

The castor seeds were collected from Sabon-Gari Market Kaduna State Nigeria and were ground into powdered form by using a simple grinder machine.

Oil extraction

The castor oil was extracted using soxhlet extractor. About 500 ml of *n*-hexane was poured in a round bottom flask and 100 g of ground castor seed packed in a filter paper was placed in the thimble according to AOAC (2000) with modification.

Transesterification reaction

Transesterification reaction was carried out in screw-capped vials placed inside a reciprocal shaker. The initial reaction mixture consisted of castor oil: ethanol molar ratio of 1:7.14 lipozyme (40 U) immobilized from *Mucormiehei* and was stirred at 200 rpm along with the respective controls according to Kumari et al. (2009)

Design of Experiments

Central composite design integrated in response surface methodology (RSM) provided in the Design-Expert 7.1.4 (Stat-Ease, Inc) was employed to design the experiments and fit a quadratic response surface to the experimental data (Chin et al., 2009).The response Y, was the yield of biodiesel. The factors chosen were oil: ethanol ratio (A), lipozyme concentration (B), reaction time (C) and temperature (D).The impeller speed was fixed at 200 rpm. The yield) was fitted to a second-order model in order to correlate the response variable with the independent variable

Analysis of the reaction products

The percentage conversion (%) of ethyl ester was measured by determining the remaining unreacted fatty acid in the reaction mixture by titration with NaOH (0.1M). The percentage conversion (%) of ethyl ester was calculated using the formula below.

$$Conversion of methyl ester (\%) = \frac{Vol. of NaOH used without enzyme - Vol. of NaOH used with enzyme}{Vol. of NaOH used without enzyme} x\ 100$$

Characterization of the biodiesel produced

The fatty acid ethyl ester was characterized for specific gravity using specific gravity bottle, viscosity was determined using viscometer (NDJ-5A) model, refractive index using Abbe's refractometer (Model AR-001). The cetane number of the produced biodiesel was determined according to Krisnangkura(1989). Calorific value was measured according to the method of Gerpen (2005), Flash point was determined according to ASTM D 93 (2000). The cloud points was determined according to ASTM D2500 (2000). Acid value, iodine and saponification number were determined by titrimetric method according to AOAC (2000).

Results

The highest biodiesel yield of 93.0% and 75.53% was obtained for experimental and predicted responses respectively in run 18. The lowest response of 5.0 % was recorded at run 23 with the predicted being 10.78% (Table). The final model equation in terms of actual factors is given in equation 1:

Sqrt(Yield)=-41.35648+109.52257×
Oil/EOH +1.68536×lipozyme+0.14607×
Time +2.79340×Temperature +297.52604×
Oil/EOH2-0.011360×Lipozyme2-
4.746566E-004×Time2-0.030278 ×
Temperature2-2.16146×Oil/EOH×
Lipozyme-0.40162 *Oil/EOH×Time +
0.66875*Oil/EOH×Temperature-
2.11574E-003 ×Lipozyme×Time-
3.60833E-003 ×Lipozyme×Temperature+
7.46296E-004 ×Time×Temperature --------------------(1)

The results of the analysis of variance shows that the model F-value of 13.01 with *p*- value of < 0.0001. The terms B, C, B^2, C^2 , D, D^2, AB and BC were significant model terms by having "prob > F" less than 0.050. While A, A^2 AC, AD, BD and CD were not significant model terms by having *p*-values greater than 0.050. The R2 value was0.92 (Table 2)

Table 1: Experimental and predicted responses for central composite second-order design

Run order	Oil/ethanol ratio	Lipozyme (U/ml)	Time (minutes)	Temperature (°C)	Predicted yield (%)	Actual yield (%)
1	0.02	10.00	30.00	25.00	32.02	38.00
2	0.10	10.00	30.00	25.00	42.28	34.80
3	0.02	70.00	30.00	25.00	77.60	70.00
4	0.10	70.00	30.00	25.00	77.49	81.60
5	0.02	10.00	300.00	25.00	26.33	20.60
6	0.10	10.00	300.00	25.00	27.92	32.50
7	0.02	70.00	300.00	25.00	37.64	52.30
8	0.10	70.00	300.00	25.00	28.85	20.10
9	0.02	10.00	30.00	75.00	20.28	16.70
10	0.10	10.00	30.00	75.00	33.22	19.10
11	0.02	70.00	30.00	75.00	55.04	51.00
12	0.10	70.00	30.00	75.00	57.60	51.00
13	0.02	10.00	300.00	75.00	24.67	21.10
14	0.10	10.00	300.00	75.00	28.93	24.20
15	0.07	70.00	300.00	75.00	25.15	20.30
16	0.10	70.00	300.00	75.00	13.16	13.60
17	0.02	40.00	165.00	50.00	19.04	74.00
18	0.14	40.00	165.00	50.00	75.53	93.00
19	0.06	20.00	165.00	50.00	16.96	25.40
20	0.06	100.00	165.00	50.00	52.65	56.00
21	0.06	40.00	105.00	50.00	63.23	74.00
22	0.06	40.00	435.00	50.00	18.98	20.00
23	0.06	40.00	165.00	75.00	10.78	5.00
24	0.06	40.00	165.00	100.00	10.77	6.80
25	0.06	40.00	165.00	50.00	75.70	76.20
26	0.06	40.00	165.00	50.00	75.70	76.00
27	0.06	40.00	165.00	50.00	75.70	76.00
28	0.06	40.00	165.00	50.00	75.70	77.00
29	0.06	40.00	165.00	50.00	75.70	70.00
30	0.06	40.00	165.00	50.00	75.70	79.00

Table 2: Analysis of variance of the quadratic model developed in the design of experiments

Parameters	Sum of Squares	Mean of Square	F- value	Prob>F
Source model	19901.54	1421.54	13.01	< 0.0001
A	25.83	25.83	0.24	0.6338
B	1909.95	1909.95	17.4	0.0008
C	2937.09	2937.09	26.88	0.0001
D	696.60	696.60	6.37	0.0233
A^2	6.22	6.22	0.057	0.08147
B^2	2867.09	2867.09	26.24	0.0001
C^2	2051.78	2051.78	18.78	0.0006
D^2	9822.62	9822.62	89.89	0.0001
AB	107.64	107.64	0.99	0.03367
AC	75.26	75.26	0.69	0.4196
AD	7.16	7.16	0.065	0.8015
BC	1174.78	1174.78	10.75	0.0015
BD	117.18	117.18	1.07	0.3168

Figure 1 shows the 3D plot for the interaction of oil: ethanol ratio and lipozyme concentration on biodiesel yield. The lower and higher levels of lipozyme did not result in higher yield of biodiesel, but maximum biodiesel yield was obtained at optimum lipozyme concentration. Figure 1 (b) shows that the biodiesel yield increased with increase in oil: ethanol ratio. The yield decreased with increase in the incubation time. Figure 1 (c) shows the 3D plot for the interaction of oil: ethanol ratio and temperature. The yield increased with the increase in oil: ethanol ratio. Figure 1 (d) shows that at lower and higher levels of lipozyme concentration the biodiesel yield did not increase. However at optimum lipozyme concentration, a maximum biodiesel yield was obtained. Figure 1(e) shows that at lower and higher levels of lipozymeconcentration the biodiesel yield did not increase. However at optimum lipozyme concentration, a maximum biodiesel yield was obtained, but the yield decreased with increase and decrease in temperature. Figure 1 (f) shows the 3D plot for the interaction of incubation time and temperature on biodiesel yield.

Table 3 shows some fuel properties of biodiesel produced. The specific gravity was 0.91 and refractive index was 1.41 $\pm$ 0.01. The biodiesel had the viscosity of 14.1, the calorific value of 38.0 $\pm$ 0.10 mJ/ kg and cetane number of 53.9. The flash point and cloud point were 150^{0}C and 7^{0}C respectively. The iodine value was 101.0 $\pm$ 0.53 gI2/100?g, acid value was 0.57 $\pm$ 0.01 mg KOH/g and saponification value was 180 $\pm$ 0.25 mg KOH/g respectively.

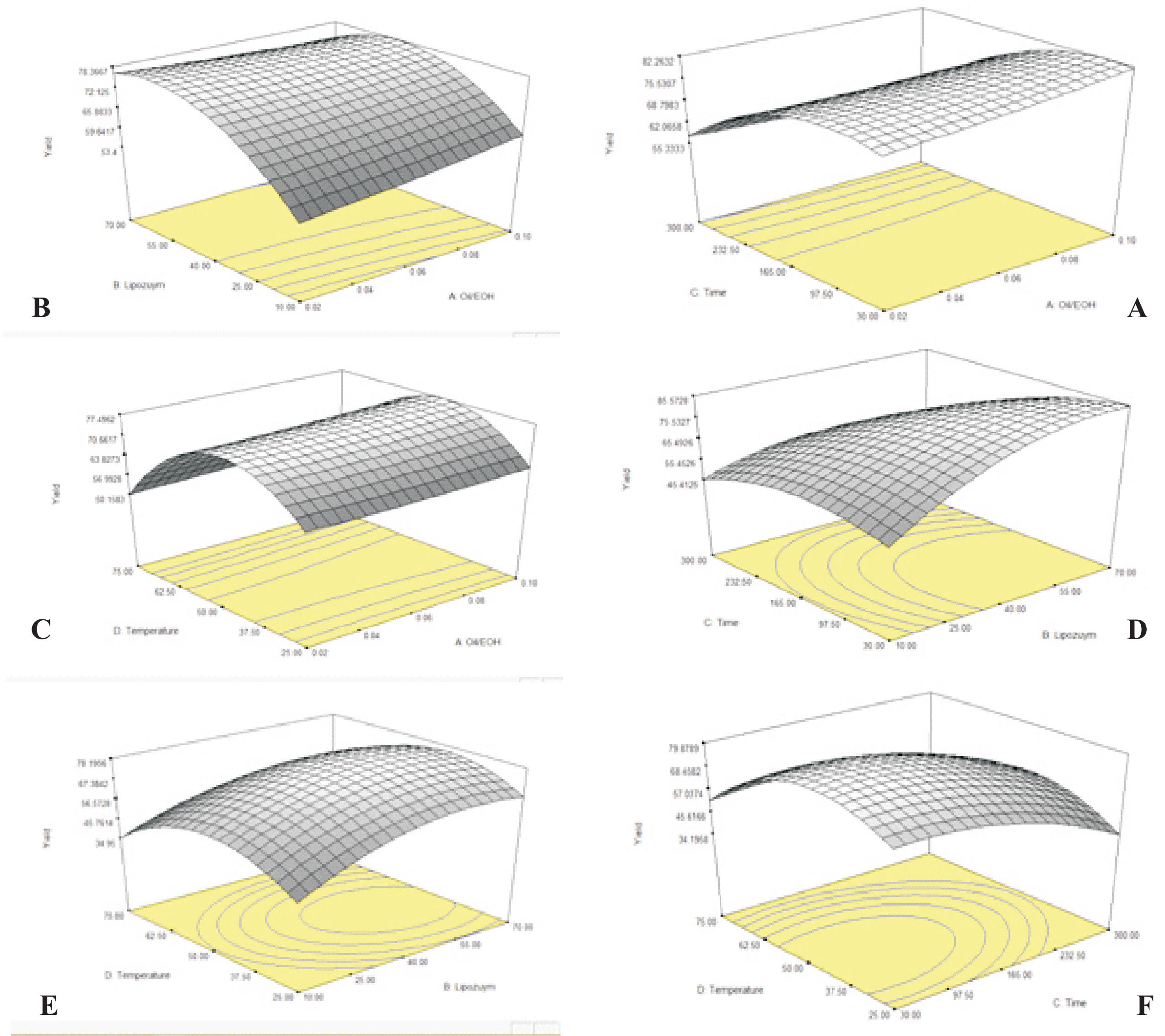

Figure 1: A three dimensional response surface plot of (a) the effect of oil: ethanol ratio and lipozyme concentration (b) the effect of oil: ethanol ratio and incubation time (c) the effect of oil: ethanol ratio and temperature (d) the effect of lipozyme concentration and incubation time (e) the effect of lipozyme concentration and temperature (f) the effect incubation time and temperature on biodiesel yield

Table 3. Physicochemical properties of castor oil seed biodiesel

Properties	Castor seed ethyl ester	Diesel	ASTM D6751
Biodiesel yield (%)	93.0	-	-
Specific gravity	0.91		-
Refractive index	1.41±0.01		
Viscosity at 40°C (Cs	14.1	2.8	1.9-6
Calorific value (MJ/kg)	38.0±0.10	45	
Cetane number	53.9	52	
Flash point ^{0}C	150		93 minimum
Cloud point ^{0}C	7	-12	
Iodine value g I_2/100?g	101±0.53		
Acid value (mg KOH/g)	0.57±0.01	-	0/5 maximum
Saponification value (mg KOH/g)	180±0.25		

Discussion

In each of the three dimensional plots, the interaction effect of the two parameters was plotted while the third and fourth parameters were fixed at the medium values. The decrease in biodiesel yield at higher oil ethanol ratio could be due to separation problem resulting from excessive ethanol, or in activation of the enzyme by ethanol (Molla and Nigus, 2014).The decrease in biodiesel yield at high lipozyme concentration and oil ethanol ratio could be that, in the presence of a high amount of lipase because the enzyme active site cannot be exposed to the substrates and many molecules of the enzyme aggregate together and thus results in low biodiesel yield (Liou et al., 1998). The elliptical nature of the 3D plots shows the significance of the interactions of variables on biodiesel yield (Samukawa et al., 2000).Bello and Makanju (2011) used ethanol; oil molar ratio of 6 to 1 and obtained the biodiesel yield of 92% after 3 hours of stirring from castor oil.

The analysis of variance for the quadratic model revealed that lipozyme concentration, temperature, incubation time with their quadratic coefficients were the significant factors in biodiesel production. The value of the regression coefficient indicates that the quadratic model was able to predict almost 92.39 % of the total variance of the system. The model F-value of 13.01 implies the model is significant and indicates that only a 0.01% chance that a "model F-value" this large could occur due to noise.The optimized condition for biodiesel production were oil/ethanol ratio (1:7.14), (1.2 ml), lipozyme concentration (40 U) incubation time of (165 min) and temperature 50^{o}C.

The high viscosity of the fuel reduces the atomization but this issue can be handled with the use of blends with petro-diesel (Deep et al., 2017).

The result shows the less likelihood of the biodiesel produced to ignite accidentally and could be safely handled for storage owing to its high flash point. The low cloud point helps in keeping the biodiesel in liquid condition which makes transportation easier. The lower calorific value could be attributed to the presence of chemically bound oxygen in the fatty acid chains (Srivastava and Prasad, 2000). Aldo et al. (2003) reported the calorific value of 30.4 mJkg^{-1} in castor oil biodiesel.The molecular weight, fatty acid chain length, degree of unsaturation and degree of conjugation determine the refractive index of biodiesel (Sadrolhossein et al.,2011).

Conclusion

The analysis of variance for the quadratic model revealed that lipozyme concentration, oil methanol ratio, temperature and incubation time are the significant factors in biodiesel production from castor oil. The properties of the biodiesel produced were largely in conformity with ASTM D6751standards

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