Research Article

Biodiesel production from jatropha curcas seeds by reactive extraction: Optimization study using central composite design

Zaharaddeen N. Garba,[1*] S. E. Abechi,[1] Benedict O. Odjobo[2] and Amina A. Nwokedi[3]

[1]Department of Chemistry, Ahmadu Bello University, P.M.B. 1044, Zaria, Nigeria
[2]Federal Institute of Industrial Research Oshodi (FIIRO), Lagos, Nigeria
[3]School of Chemical Engineering, Engineering Campus, Universiti Sains, Malaysia, 14300 Nibong Tebal, Penang, Malaysia

Abstract

This research work investigates the optimum conditions for the production of biodiesel from jatropha curcas seeds by reactive extraction. The reactive extraction to convert jatropha seed oil to biodiesel was carried out in a round bottom flask equipped with a reflux system, magnetic stirrer and heater. Ethanol and H_2SO_4 were used as solvent and catalyst respectively. The experimental design selected for this study was using a central composite design (CCD) that helps in investigating linear, quadratic, cubic and two-factor interaction effects of the four process parameters (independent variables). The response parameter of the study was the biodiesel yield. The parameter with the most significant effect on the fatty acid ethyl esters (FAEE) yield is catalyst loading parameter (X_4) followed by the reaction time (X_1) reaction temperature (X_2) and the ethanol to seed ratio (X_3) having the least significant effect based on their F values of 120.52, 106.91, 5.99 and 2.58 respectively. The interactive studies show that the effect of time on the reaction is more prominent at higer catalyst loading. The experimental values obtained were in good agreement with the values predicted by the models.
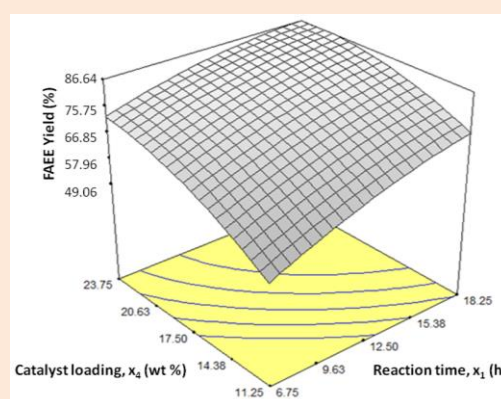
*Correspondence
Author: Zaharaddeen N. Garba
Email: dinigetso2000@gmail.com

Introduction

Biodeiesel also known as fatty acid methyl esters is derived from triglycerides by transesterification with short chain of alcohol in the presence of a catalyst [1]. It attracted considerable attention since the past decades as an alternative fuel [2] with similar physical properties such as octane number, energy content and viscosity to those of petroleum-derived diesel fuel [3]. Biodiesel fuels contain approximately 10% by weight of oxygen according to Dorado et al., 2003 [4] and combustion is better, compared to conventional diesel. In addition, this fuel is biodegradable, renewable, clean and non-toxic when compared to petroleum-derived diesel [5]. The use of biodiesel is expected to help reduce the use of fossil fuel and indirectly reduce the emissions of green house gases.

Several studies have reported the conversion of edible oils into fatty acid alkyl esters (biodiesel). These includes edible oils such as palm oil [6–8], rapeseed oil [9], sunflower oil [10] and coconut oil [11]. Edible oils are abundantly available in the market; hence they are extensively used as viable feedstock for biodiesel production. Some of these oils, for example palm oil, are also cheap, making them economically feasible as feedstock. However, the utilization of edible oils in the production of biodiesel has generated concerns as it is a threat to the world effort at ensuring food security around the globe. The need for a search for alternative oil sources (feedstock) particularly non-edible oils for biodiesel production is therefore a necessity. There are a few non-edible oils that have been identified

for biodiesel production. They includes sea mango oil [12], waste cooking oil [13–15], cotton oil [16] and algae oil [17–20].

Jatropha curcas is an ornamental, medicinal and multipurpose shrub belonging to the Euphorbiaceace family [21]. It has been a subject of interest by many researchers, particularly in the biodiesel area [22]. It is a promising raw material for biodiesel production, because the seed oil content is potentially high, at 35–55% of the seed dry weight, and it has been shown to grow on marginal, arid land [23] which is not usable for food production, so may not compete for land.

Most of the biodiesel in the market are produced by conventional methods. The conventional method of transesterification reaction was used to free lipase as a catalyst in order to drive forward the reaction to form ester and glycerol [24]. The operation cost of the conventional method is usually high due to complicated steps involved in the process like hydraulic pressing, expeller pressing and solvent extraction usually using hexane, a hazardous chemical reagent that contributes to environmental pollution. To trim the cost and prevent environmental pollution, reactive extraction (or ''in situ transesterification'') is an alternative method of producing biodiesel from oil-bearing materials which only require a single step process [22].

In reactive extraction, oil-bearing materials are brought directly into contact with alkaline/acidic alcohol. The method has been applied to various oil-bearing substances, including rapeseed [25], Smyrnium cordifolium Boiss [26], soya [27], sewage [28], Chlorella salina [29] and algae [30].

The main objective of this study is therefore to produce biodiesel from Jatropha curcas by reactive extraction process in the presence of acidic catalyst and investigate the effect of four process parameters namely: reaction temperature, reaction time, catalyst loading and solvent to seed ratio on the biodiesel yield using Central Composite Design (CCD), a subset of Response Surface Methodology (RSM).

Experimental
Jatropha curcas seeds collection

Jatropha curcas seeds were collected from the Agronomy Department of the Institute of Agricultural Research, Ahmadu Bello University, Zaria, Nigeria. The seeds were stored in dark air-tight containers to prevent photo-oxidation, as well as to minimize moisture adsorption.

Treatment of jatropha curcas seeds for biodiesel production

The seeds were blended and sieved into fine solid particles (less than 1mm). It was then weighed and dried in a drying oven at 105°C for an hour [22]. The dried seeds were then sieved again to obtain particles of < 0.355 mm. In order to determine the maximum amount of oil that can be extracted from the seeds using conventional method, Soxhlet extractor with excess n-hexane as the solvent was utilized. After the extraction process, hexane was removed using rotary evaporator and the extracted oil was measured [31].

Reactive extraction

The reactive extraction to convert Jatropha seed to biodiesel was carried out in a round bottom flask equipped with a reflux system, magnetic stirrer and heater. A portion (20 g) of the dry, blended and sieved jatropha seeds were placed into a 250 ml round bottom flask. Solvent (ethanol) and the acid catalyst were then added into the round bottom flask. The reaction mixture was then pre-treated by stirring without heating for 1 hour. The mixture was then heated to 60°C for different reaction periods. Upon completion of the reaction period, the mixture was cooled and then filtered. The solid residue was washed repeatedly with methanol and the excess methanol in the filtrate was recovered using rotary evaporator. After evaporation, two layers of liquid were formed. The upper layer was dark yellow in color, containing crude biodiesel while the bottom layer was dark brown in color containing glycerol. The volume of the top layer was then measured and recorded [31]

Design of experiment (DOE) using response surface methodology (RSM)

The design of experiment (DOE) for the transesterification of the jatropha seed was developed using Design-Expert Software, version 6.0.6 (STAT-EASE Inc., Minneapolis, USA). The experimental design selected for this

study was a central composite design (CCD) with the biodiesel yield obtained from the reactive extraction as the response. The four variables studied were; reaction temperature (30–50ºC), reaction time (1–15 h), catalyst loading (5-30 wt %) and solvent to seed ratio (5-15) on the biodiesel yield.

CCD was chosen for the statistical design of the experiment because it helps in optimizing the effective parameters with a minimum number of experiments and analyzes interaction between the parameters. It is characterized by three operations namely: 2^n factorial runs, 2n axial runs and six center runs [32]. These translated into 16 factorial points, 8 axial points and 6 replicates at the center which gives a total of 30 experiments.

$$\text{Total number of experiments (N)} = 2^n + 2n + n_c \qquad (1)$$

Alpha α, the distance of the axial point from the center which makes the design rotatable has its value for this CCD fixed at two. The complete design matrix of the experiments and the results are given in **Table 1**.

Table 1 Experimental design matrix and results for the transesterification process of Jatropha curcas seed oil using H_2SO_4 catalyst

Run	Block type	Transesterification process variables				FAEE yield (%)
		Reaction time (h)	Reaction temperature (ºC)	Ethanol/seed ratio	Catalyst loading (wt %)	
1	Fact	6.75	65.00	12.50	23.75	73.74
2	Fact	18.25	55.00	12.50	23.75	76.10
3	Fact	18.25	65.00	7.50	11.25	66.79
4	Fact	18.25	65.00	12.50	11.25	71.10
5	Fact	6.75	65.00	12.50	11.25	58.99
6	Fact	18.25	65.00	12.50	23.75	84.09
7	Axial	12.50	60.00	5.00	17.50	72.93
8	Center	12.50	60.00	10.00	17.50	76.63
9	Fact	18.25	55.00	7.50	11.25	67.38
10	Fact	6.75	65.00	7.50	23.75	72.57
11	Axial	12.50	70.00	10.00	17.50	75.40
12	Axial	12.50	60.00	10.00	30.00	82.32
13	Fact	6.75	55.00	12.50	11.25	45.25
14	Fact	18.25	65.00	7.50	23.75	75.76
15	Axial	12.50	50.00	10.00	17.50	67.62
16	Center	12.50	60.00	10.00	17.50	75.36
17	Fact	6.75	55.00	12.50	23.75	69.37
18	Axial	1.00	60.00	10.00	17.50	42.69
19	Fact	6.75	55.00	7.50	11.25	43.40
20	Center	12.50	60.00	10.00	17.50	76.23
21	Fact	6.75	55.00	7.50	23.75	68.55
22	Axial	24.00	60.00	10.00	17.50	91.17
23	Axial	12.50	60.00	10.00	5.00	38.34
24	Center	12.50	60.00	10.00	17.50	75.49
25	Axial	12.50	60.00	15.00	17.50	79.83
26	Fact	6.75	65.00	7.50	11.25	51.21
27	Fact	18.25	55.00	12.50	11.25	68.11
28	Center	12.50	60.00	10.00	17.50	76.12
29	Center	12.50	60.00	10.00	17.50	75.85
30	Fact	18.25	55.00	7.50	23.75	82.88

Table 2 Range and levels of the transesterification process variables

Variables	Code	Unit	Coded variable levels				
			$-\alpha$	-1	0	$+1$	$+\alpha$
Reaction time	x_1	h	1.00	6.75	12.50	18.25	24.00
Reaction temperature	x_2	ºC	50.00	55.00	60.00	65.00	70.00
Ethanol/seed ratio	x_3	–	5.00	7.50	10.00	12.50	15.00
Catalyst loading	x_4	wt %	5.00	11.25	17.50	23.75	30.00

All variables at zero level constitute the center points, the two level independent variables were coded as +1 and -1 for high and low values respectively and were used to represent the 16 factorial points while the combination of each of the variables at either its lowest ($-\alpha$) level or highest ($+\alpha$) level with the other variables at zero level constitutes the axial points [12]. **Table 2** lists the range and levels of the four independent variables studied.

The rotatability value α, which depends on the number of points in the factorial portion of the design, was obtained using equation 2 [32]:

$$\alpha = N_P^{1/4} \qquad (2)$$

where $N_P = 2^n$ is the number of points, n is the number of factors.

Optimal conditions for the response (yield of the biodiesel) were determined using the optimal predictor quadratic model as shown in equation 3:

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i\right)^2 + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} b_{ij} x_i x_j \qquad (3)$$

where Y is the predicted response, b_o is the constant coefficients, b_{ii} the quadratic coefficients, b_{ij} the interaction coefficients and x_i, x_j are the coded values of the activated carbon preparation variables considered. The quality of the fit of polynomial model was expressed by the correlation coefficient (R^2). The model F-value (Fisher variation ratio), probability value (Prob > F), and adequate precision (AP) are the main indicators demonstrating the significance and adequacy of the used model [33].

The same software (Design-Expert) was used for the regression analysis of the experimental data to fit the second order polynomial equation and also for the evaluation of the statistical significance of the equation developed [12].

Analysis

The composition and yield of fatty acid ethyl esters (FAEE) of biodiesel in the upper layer of the reactive extraction products were analyzed using gas chromatography (Perkin–Elmer, claurus 500) equipped with flamed ionized detector (FID) and capillary column (15 m x 0.53 mm; 0.5 lm film). n-Hexane was used as the solvent while helium was used as the carrier gas. The oven temperature was set at 110ºC and then increased to 220ºC at a rate of 10ºC/min. The temperature of the detector and injector were set at 220 and 250ºC, respectively. Methyl heptadecanoate was used as the internal standard. The peaks of different ethyl esters were identified by comparing the retention time of each component in the reaction samples with the peaks of pure ethyl ester standard compound.
The yield of the biodiesel in the samples was calculated as

$$\text{Yield (\%)} = \frac{\sum(\text{Concentration of each component}) \times (\text{Volume of upper layer})}{\text{Total weight of oil in the sample}} \times 100 \qquad (4)$$

The biodiesel preparation was meticulously adhered to the DOE table as shown in Table 1.

Results and discussion
Design of experiments using CCD

The development of a polynomial regression equation for analysis of correlation of the FAEE yield was done using CCD, the results are shown in Table 1. The observed percentage yield ranged between 38.34 to 91.17 % with the sequential model sum of squares being a quadratic correlation as suggested by the DOE software. The selection was based on the highest order of polynomial where the model was not aliased and additional terms were significant. As presented in **Figure 1**, the correlation (R^2) between experimental and predicted data was 0.9500 (Y_{FAEE}) which is within desirability range as has been reported in literature [32].

The R^2 value was relatively high and in reasonable agreement with adjusted and predicted R^2 (Adj. and Pred. R^2) values of 0.9033 and 0.7129 respectively, with standard deviation (S.D.) of 4.07. The resulting model equation for Y_{FAEE} after eliminating the insignificant parameters is given as:

$$Y_{FAEE} = 75.95 + 8.59x_1 + 2.03x_2 + 9.12x_4 - 2.52x_1^2 - 4.17x_4^2 - 2.50x_1x_4 \tag{5}$$

Analysis of variance (ANOVA)

The ANOVA of the FAEE yield model gave a significant F-value of 20.35 as shown in **Table 3** with a 0.01 % chance of variation due to noise (effect of some uncontrollable factors on normal operating conditions causing some induced variations). Prob > F values less than 0.0001, further indicated the model term's significance. In this case $x_1, x_2, x_4, x_1^2, x_4^2$ and x_1x_4 were the significant terms with $x_3, x_2^2, x_3^2, x_1x_2, x_1x_3, x_2x_3, x_2x_4$ and x_1x_4 as the insignificant terms. Adequate Precision (AP) measures the signal to noise ratio. A ratio greater than 4 is desirable [33]. In this case, ratio of 15.19 for FAEE yield indicated an adequate signal which implies that this model can be used to steer the design space.

It is observed from Table 3 that the parameter with the most significant effect on the FAEE yield is catalyst loading parameter (X_4) followed by the reaction time (X_1) with reaction temperature (X_2) and the ethanol to seed ratio (X_3) having the least significant effect based on their F values of 120.52, 106.91, 5.99 and 2.58 respectively.

Single parameter effect
Effect of catalyst loading (X_4)

Figure 2 show the influence of catalyst loading on the FAEE yield. The highest yield was obtained using catalyst loading of 23.75 wt % with a yield of about 84 %.
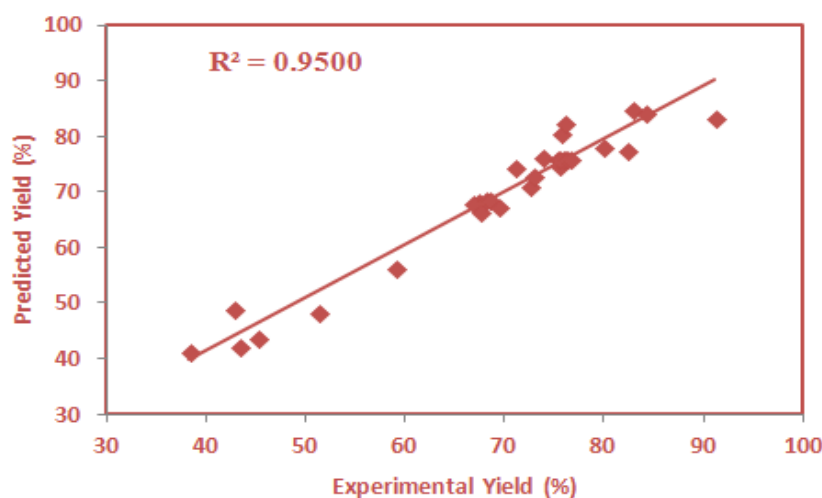

Figure 1 The correlation (R^2) between experimental and predicted data.

Table 3 Analysis of variance (ANOVA) for the regression model equation and coefficients

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob>F
Model	4716.30	14	336.88	20.35	< 0.0001
x_1	1769.69	1	1769.69	106.91	< 0.0001
x_2	99.11	1	99.11	5.99	0.0272
x_3	42.64	1	42.64	2.58	0.1294
x_4	1994.97	1	1994.97	120.52	< 0.0001
x_1^2	173.99	1	173.99	10.51	0.0055
x_2^2	51.66	1	51.66	3.12	0.0976
x_3^2	0.65	1	0.65	0.04	0.8450
x_4^2	476.43	1	476.43	28.78	< 0.0001
$x_1 x_2$	44.47	1	44.47	2.69	0.1220
$x_1 x_3$	1.59	1	1.59	0.10	0.7612
$x_1 x_4$	99.63	1	99.63	6.02	0.0269
$x_2 x_3$	38.98	1	38.98	2.35	0.1457
$x_2 x_4$	13.48	1	13.48	0.81	0.3811
$x_3 x_4$	7.75	1	7.75	0.47	0.5042
Residual	248.30	15	16.55	–	–

S.D.	4.07	R^2	0.9500	Adj. R^2 0.9033
A.P.	15.19	Mean	69.38	Pred. R^2 0.7129
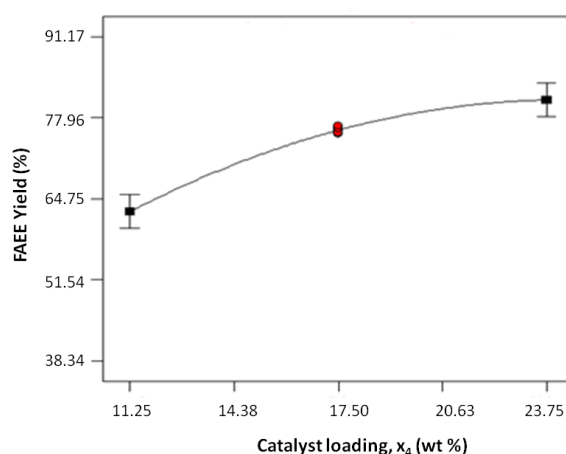
Figure 2 The effect of catalyst loading on the FAEE yield.

As can be seen, the FAEE yield showed a linear relation with the catalyst loading by increasing tremendously from about 60 to 84.08 % when the catalyst loading also increased from 11.25 to 23.75 wt % with other parameters being a time of 12.5 h, temperature of 60 °C and ethanol to seed ratio of 10.00. This linear relation is possible due to the fact that increased number of catalyst molecules were able to boost the reaction [34].

Effect of reaction time (X_1)

Figure 3 show the effect of reaction time on the FAEE yield with the remaining process parameters fixed at a temperature of 60°C, 10.00 ethanol to seed ratio and catalyst loading of 17.50 wt %. It was observed from the Fig. that FAEE yield increased with increase in the reaction time. As the reaction time increased from 6.75 to 18.25 hrs, the

FAEE yield also increased significantly from 64.75 to about 84 %. The results are similar to those obtained in literature [35].

Effect of reaction temperature (X₂)

Figure 4 show the effect of reaction temperature on the FAEE yield with reaction time, ethanol to seed ratio and catalyst loading fixed at 12.50 hrs, 10.00 and 17.50 wt % respectively.

In this work, the reaction temperature was studied between 50 to 70°C as shown in Table 2. The FAEE yield was found to increase from about 70 to 78 % when the reaction temperature increased from 55°C to 65°C as can be observed from the Figure, this linear relation between the FAEE yield and the reaction temperature suggested the endothermic nature of the process.

Effect of Ethanol to seed ratio (X₃)

Figure 5 show the effect of ethanol to seed ratio on FAEE yield with the remaining parameters fixed at a reaction time of 12.50 hrs, temperature of 60°C and catalyst loading of 17.50 wt %.

It can be seen from the Figure that FAEE yield remained almost constant even after increasing the ethanol to seed ratio from 7.50 to 12.50. This is because for higher ratios, the separation of glycerol is difficult due to excess ethanol which hinders the decantation by gravity so that apparent yield of biodiesel decreases since part of the glycerol remains in the biodiesel phase. Another reason is when glycerol remains in solution, it helps to drive the equilibrium back to the left, lowering the yield [36].
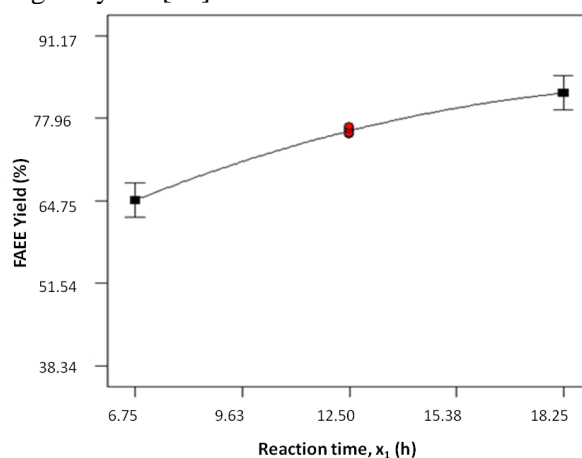

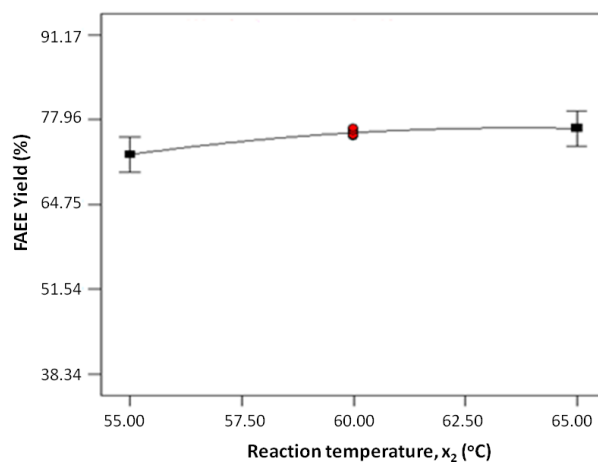**Figure 3** The effect of reaction time on the FAEE yield.

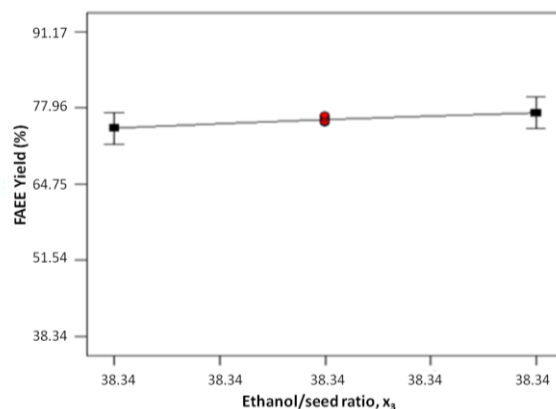**Figure 4** Effect of reaction temperature on the FAEE yield

Figure 5 Effect of ethanol to seed ratio on FAEE yield

Interaction effect

The only significant interaction parameter from the ANOVA table was the interaction between reaction time and catalyst loading ($X_1 X_4$) based on their F and Prob > F values of 6.02 and 0.027 respectively. **Figure 6** shows the interaction effect between the reaction time and catalyst loading with reaction temperature and ethanol to seed ratio fixed at 60ºC and 10 respectively. As expected and explained previously, higher reaction time allows the transesterification to proceed to completion which result in to higher yield. It can be seen from Fig. 6 that effect of reaction time is more prominent at higher catalyst loading because at catalyst loading of 23.75 wt %, the FAEE yield increase rapidly with longer reaction time but the increase in FAEE yield is much slower at a low catalyst loading of 11.25 wt %. This revealed that the reaction rate increases much faster with higher catalyst loading as the increase in number of catalyst molecules boast up the reaction rate.

Optimization analysis

CCD was used to optimize the parameters affecting the FAEE yield responses. The function of desirability was applied using Design-Expert software (Stat-Ease, Inc., Minneapolis, MN 55413, USA) for the optimization. The target criterion was set as maximum value for the response while the values of the variables were set in the ranges being studied. The predicted and experimental results for the FAEE yield obtained at optimum conditions are shown in **Table 4**. It was observed that the experimental values obtained were in good agreement with the values predicted from the models, with relatively small error of 3.20 % between the predicted and the experimental values.
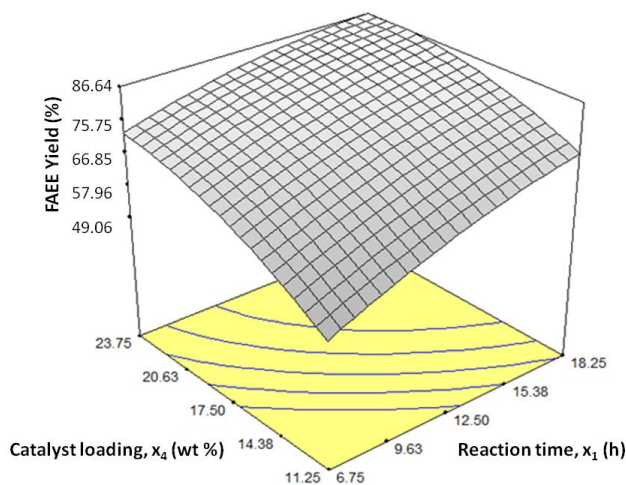

Figure 6 Three-dimensional response surface plot of the interaction effect between the reaction time and catalyst loading

Table 4 Model validation

Model desirability	Reaction time, X_1(h)	Reaction temperature, X_2 (ºC)	Ethanol to seed ratio, X_3	Catalyst loading, X_4 (wt %)	FAEE Yield (%)		
					Predicted	Experimental	Error
0.89	18.25	62	12.40	21.60	85.29	88.02	3.20

Conclusions

A central composite design was used to optimize the production of biodiesel by reactive extraction process using ethanol and H_2SO_4 as solvent and catalyst respectively. The parameters optimized were reaction temperature, reaction time, catalyst loading and solvent to seed ratio with the response being FAEE yield. The yield of 85.29 % was obtained by using reaction temperature of 62ºC, reaction time of 18.25 hrs, catalyst loading of 21.62 wt % and solvent to seed ratio of 12.50. It was observed that the experimental values obtained were in good agreement with the predicted values from the models with relatively small error. The parameter with the most significant effect on the FAEE yield is catalyst loading followed by the reaction time with reaction temperature and ethanol to seed ratio having the least significant effect based on their F values of 120.52, 106.91, 5.99 and 2.58 respectively.

References

[1]   K.T. Tan, M.G. Meei, T.L. Keat, M. Abdul Rahman, The J. Supercrit. Fluids 53, 2010, 82–87.
[2]   G.V. Kim, W.Y. Choi, D. Kang, S.Y. Lee, H.Y. Lee, BioMed. Res. Intl., 2014, 1–11.
[3]   D.H. Qi, H. Chen, L.M. Geng, Y.Z.H. Bian, X.C.H. Ren, App. En. 87, 2010, 1679–1686.
[4]   M.P. Dorado, E. Ballesteros, J.M. Arnal, J. Gomez, F.J. Lopez, Fuel 82, 2003, 1311–1315.
[5]   J.C. Pasqualino, D. Montane, J. Salvado, Synergetic effects of biodiesel in the biodegradability of fossil-dreived fuels, Biom. Bioen. 30, 2006, 874–879.
[6]   M.A. Kalam, H.H. Masjuki, Biom. Bioen. 23, 2002, 471–479.
[7]   J.A. Melero, L. Fernando Bautista, G. Morales, J. Iglesias, R. Sánchez-Vázquez, Chem. Eng. J. 161, 2010, 323–331.
[8]   K.F. Yee, J. Kansedo, K.T. Lee, Chem. Eng. Comm. 197, 2010, 1597–1611.
[9]   U. Rashid, F. Anwar, Fuel 87, 2008, 265–273.
[10]   G. Guan, N. Sakurai, K. Kusakabe, Chem. Eng. J. 146, 2009, 302–306.
[11]   P. Nakpong, S. Wootthikanokkhan, Renew. En. 35, 2010, 1682–1687.
[12]   J. Kansedo, K.T. Lee, Chem. Eng. J. 214, 2013, 157–164.
[13]   M. Berrios, M.A. Martín, A.F. Chica, A. Martín, Chem. Eng. J. 160, 2010, 473–479.
[14]   T. Issariyakul, M.G. Kulkarni, L.C. Meher, A.K. Dalai, N.N. Bakhshi, Chem. Eng. J. 140, 2008, 77–85.
[15]   P.D. Patil, S. Deng, J.I. Rhodes, P.J. Lammers, Fuel 89, 2010, 360–364.
[16]   G. Kafuku, M.K. Lam, J. Kansedo, K.T. Lee, M. Mbarawa, Bioresour. Technol. 101, 2010, 7000–7004.
[17]   Y. Chisti, Biotechnol. Adv. 25, 2007, 294–306.
[18]   Y. Chisti, Biodiesel from microalgae beats, Trends Biotechnol. 26, 2008, 126–131.
[19]   X. Meng, J. Yang, X. Xu, L. Zhang, Q. Nie, M. Xian, Renew. En. 34, 2009, 1–5.
[20]   E. Sánchez, K. Ojeda, M. El-Halwagi, V. Kafarov, Chem. Eng. J. 176–177, 2011, 211–216.
[21]   Z.N. Garba, C.E. Gimba, P. Emmanuel, J. Phy. Sci. 24, 2013, 49–61.
[22]   F.H. Kasim, A.P. Harvey, Chem. Eng. J. 171, 2011, 1373–1378.
[23]   K. Becker, H.P.S. Makkar, Lipid Technol. 20, 2008, 104–107.
[24]   M. Nasratun, H.A. Said, A. Noraziah, A.N. Abdallah, Am. J. App. Sci. 6, 2009, 1653–1657.
[25]   Y. Ren, A. Harvey, R. Zakaria, J. Biomat. Bioen. 4, 2010, 79–86.
[26]   G. Sodeifiana, J. Azizi, S.M. Ghoreishi, The J. Supercrit. Fluids 95, 2014, 1–7.
[27]   M.J. Haas, J. Am. Oil Chem. Soc. 81, 2004, 83–89.
[28]   A. Mondala, Bioresour. Technol. 100, 2009, 1203–1210.
[29]   D. Surendhiran, M. Vijay, A.R. Sirajunnisa, J. Environ. Chem. Eng. 2, 2014, 1294–1300.

[30] E.A. Ehimen, Z.F. Sun, C.G. Carrington, Fuel 89, 2010, 677–684.
[31] S.H. Shuit, K.T. Lee, A.H. Kamaruddin, S. Yusup, Fuel 89, 2010, 527–530.
[32] Z.N. Garba, A.R. Afidah, J. Anal. App. Pyrol. 107, 2014, 306–312.
[33] Z.N. Garba, A.R. Afidah, S.A. Hamza, J. Environ. Chem. Eng. 2, 2014, 1423–1433.
[34] X. Miao, Q. Wu, Bioresour. Technol. 97, 2006, 841–846.
[35] M. Andro, L. Kaiwen, T. Hossein, R. Hernandez, T. French, Bioresour. Technol., 2009, 1203–1210.
[36] K. Krisnamgkura, S. Simmaharnnop, J. Am. Oil Chem. Soc. 69, 1992, 166–169.