Statistical approach to optimization of the transesterification reaction from sorrel (*hibiscus sabdariffa*) oil

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Abstract

In an effort to optimize the reaction conditions of biodiesel production from Sorrel seed oil, Response Surface Methodology (RSM) was applied and the effects of reaction temperature, catalyst amount, reaction time and methanol/oil molar ratio, and their reciprocal interactions were ascertained. A total of 30 experimental runs were designed by Central Composite Rotatable Design (CCRD) and carried out. A quadratic polynomial was obtained for predicting the Transesterification process and the ANOVA test showed the model to be significant ($p<0.05$). The validity of the predicted model was confirmed by carrying out three independent replicates experiments. The actual maximum biodiesel yield obtained was 99.23% (w/w) at methanol/oil molar ratio 6.21, catalyst amount 1.03 (% wt.), reaction temperature 51 ^{o}C, and reaction time 63 min. The fuel properties of Hibiscus sabdariffa methylester (HSME) produced were found to be within the ASTM D6751 and DIN EN 14214 biodiesel standards. The fatty acid profile of the HSME revealed that the dominant fatty acids were oleic (58.34%), arachidic (1.55%), palmitic (18.28%) and linoleic (21.19%). Emission assessment revealed 70% reduction of CO at B80, 80% reduction of NO concentration at B40.

Key words: Biodiesel, Sorrel oil, Transesterification, Optimization, Response surface methodology

1. Introduction

Biodiesel, which is considered as an substitute of convectional diesel is gaining ground as a biodegradable, non-toxic and environment-friendly fuel to neat diesel (Knothe et al., 2005; Demirbas, 2008). It is produced through a chemical process known as “transesterification or alcoholysis” in which there is displacement of alcohol from an ester under acidic or basic catalytic conditions producing free glycerol and the fatty acid esters of the respective alcohol (Knothe et al., 2007). Biodiesel is derived from renewable feedstock like vegetable oils or animal fats. Both edible and non-edible oils have been successfully employed in biodiesel production. In Nigeria, convectional diesel is produced mainly from crude oil; however, there are alternative oil-yielding crops which can be utilized as feedstocks, such as Palm oil, *Moringa* oil, Shea butter, *Jatropha* and Coconut. Sorrel seed oil, a new competitor is emerging as a promising feedstock.

In Africa, the Sorrel seeds are hard-pressed for oil and the residual cake is cooked, seasoned with *kambo*, a local condiment. The seeds are also used for their oil in china and eaten in West Africa. In Malaysia, the seeds are used to produce scrubs and soaps. However, most of the seeds are merely discarded as by-products by the manufacturers. In Africa, the bitter seeds are roasted and grounded into powder and is used in oily soup and sauces as a meal for human consumption. Roasted seeds have been used as coffee replacement that is said to have aphrodisiac properties (Duke, 1984). According to Omobuwajo *et al*. (2000), in northern Nigeria, the seeds are fermented into a condiment known as *Mungza ntusa*. In Sudan, the seeds are used for edible oil

manufacture and the by-products of this process were used for poultry feeding Al-Wandawi *et al*. (1984). However, in a commercial sense, this oil is not in current widespread use in Nigeria, having relatively few competing medicinal and food uses.

Response surface methodology (RSM) is a useful statistical tool, which has been applied in research for optimizing various processes including transesterification reaction of vegetable oils: *Moringa oleifera* (Rashid et al., 2011), *Jatropha* oil (Tiwari et al., 2007) and cottonseed oil (Zhang et al., 2011). The main advantage of RSM is the ability to reduced number of experimental runs needed to provide sufficient information for statistically acceptable results. In this present study, an effort was made to optimize the process conditions for the transesterification step of Sorrel oil.

2.0 METHODOLOGY

2.1 *Extraction of Sorrel seed oil*

Sorrel seeds were collected from Adamawa State, Nigeria. Chaff was separated from the oilseeds by winnowing. The cleaned oilseeds were milled into powder by grinding with plate machine. A 5-liter Soxhlet apparatus and ethanol as solvent were used for the oil extraction.

2.2 *Experimental design of HSME production*

In this study, the central composite rotatable design (CCRD) was employed to optimize the HSME production. Five-level-four-factors design was applied, which generated 30 experimental runs. This included 16 factorial points, 8 axial points, and 6 central points to provide information regarding the interior of the experimental region, making it possible to evaluate the curvature effect. Selected factors for the transesterification process from the Sorrel seed oil were reaction temperature (X_1), catalyst amount (X_2), reaction time (X_3) and methanol/oil molar ratio (X_4). The coded levels of the independent factors are given in Table 1. The experiments were randomizes to minimize the effects of unexplained variability in the observed response due to extraneous factors.

2.3 *Experimental procedure*

Base catalyst transesterification reaction was applied for the HSME production, due to the low FFA value of the seed oil. A known weight of NaOH pellet was dissolved in a known volume of anhydrous methanol and was quickly transferred into the seed oil in the reactor and the reaction was monitored according to the design variables. At the completion of the reaction, the product was transferred to a separating funnel for glycerol and HSME separation. Glycerol was tapped off and the HSME left was washed with distilled water to remove residual catalyst, glycerol, methanol and soap. The washed HSME was further dried over heated $CaCl_2$ powder. The HSME yield was determined gravimetrically as described in Eqn.1

$$AIME\ yield = \frac{weight\ of\ HSME\ produced}{weight\ of\ Sorrel\ oil\ used} \quad (1)$$

2.4 *Statistical Data Analysis*

HSME production data was analyzed statistically using RSM, so as to fit the quadratic polynomial equation generated by the Design-Expert software version 8.0.3.1 (Stat-Ease Inc., Minneapolis, USA). To correlate the response variable to the independent factors, multiple regressions was used to fit the coefficient of the polynomial model of the response. The quality of the fit of the model was evaluated using test of significance and analysis of variance (ANOVA). The fitted quadratic response model is given by Eqn. 2.

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i<j}^{k} b_{ij} X_i X_j + e \quad (2)$$

Where, Y is response factor (HSME), b_o is the intercept value, b_i (i= 1, 2, …, k) is the first order model coefficient, b_{ij} is the interaction effect, and b_{ii} represents the quadratic coefficients of X_i, and e is the random error.

2.5 *Oil and fuel properties*

Fuel properties namely, moisture content, specific gravity, kinematic viscosity at 40 ^oC, iodine value, acid value, saponification value, higher heating value, flash point, cloud point and cetane number of both Sorrel seed oil and HSME were determined following standard methods and compared with American and European standards (ASTM and DIN EN 14214).

2.6 *Emissions Assesment*

In order to test the suitability of the HSME produced in I.C engine as well as compare the emissions with that of neat diesel (AGO), B10, B20, B30..... B90 blends of pure HSME with AGO at different loads (0-2.7 kW) was used, 100% AGO and 100% HSME were burnt in succession and emissions such as CO and NO were measured with with the aid of TORIX gas analyzer.

3.0 RESULTS AND DISCUSSION

3.1 *Properties of the extracted Sorrel seed oil*

The analysis of the oil showed that it has a moisture content of 0. 065%%, specific gravity of 0.886 and viscosity of 15.40 cP. The acid value of the oil was 0.80 mg KOH/g oil while the iodine value was 97.77 g I2/100g oil. Whereas the saponification value of the oil was 197.75 mg KOH/g oil, its higher heating value and cetane number were 39.86 MJ/kg and 51.90, respectively. These results are within the ranges earlier reported in the literature (Nakpong and Wootthikanokkhan, 2010; Bouanga-Kalou *et al.*, 2011).

3.2 *Optimization of the transesterification step*

Table 2 depicts the coded factors considered in this study with experimental results, predicted values as well as the residual values obtained. The highest HSME yield obtained was 99.30 % (w/w) at reaction temperature 60 ^{o}C, catalyst amount 0.90% (w/w), reaction time 50 min and methanol/oil molar ratio 6:1, while the lowest HSME yield of 89.29% (w/w) was observed at reaction temperature 60 ^{o}C, catalyst amount 0.70% (w/w), reaction time 50 min and methanol/oil molar ratio 6:1. Design Expert 8.0.3.1 software was employed to evaluate and determine the coefficients of the full regression model equation and their statistical significance. Table 3a shows the results of test of significance for every regression coefficient. The results showed that the p-value of the model terms were significant, i.e. $p < 0.05$. In this case, the four linear terms (X_1, X_2, X_3, X_4), five cross-products (X_1X_2, X_1X_3, X_1X_4, X_2X_3, X_3X_4) and the four quadratic terms (X_1^2, X_2^2, X_3^2 and X_4^2) were all remarkably significant model terms at 95% confidence level except X_2X_4. However, all other model terms were more significant than both X_4 and X_1X_2. In order to minimize error, all the coefficients were considered in the design. Table 3b shows the analysis of variance (ANOVA) of the regression equation. The model F-value of 361.87 implied a high significant for the regression model (Yuan et al., 2008). The goodness of the fit of a model was checked by the coefficient of determination (R^2). R^2 should be at least 0.80 for the good fit of a model (Guan and Yao, 2008). The R^2 of 0.9941 in this case indicated that the sample variation of 99.41% for HSME yield was attributed to the independent factors and only 0.59% of the total variation are not explained by the model. The value of adjusted determination coefficient (Adj. R^2 = 0.9962) was also very high, supporting a high significant of the model (Khuri and Cornell, 1987) and all p-value coefficients were less than 0.0001, which implied that the model proved suitable for the adequate representation of the actual relationship among the selected variables. The lack-of-fit term of 0.9589 was not significant relative to the pure error. The final equation in terms of coded factors for the response surface quadratic model is expressed in Eqn. (3).

$$Y(w/w\ \%) = 98.91 + 0.95X_1 + 1.88X_2 + 0.60X_3 + 0.13X_4 + 0.14X_1X_2 - 0.27X_1X_3 + 0.87X_1X_4 - 0.45X_2X_3 - 0.061X_2X_4 + 0.56X_3X_4 - 1.70X_1^2 - 1.44X_2^2 - 1.75X_3^2 - 1.90X_4^2 \quad (3)$$

All the X_1, X_2, X_3, X_4, X_1X_2, X_1X_4 and X_3X_4 had positive effect on the HSME yield while the rest had negative influence on the yield (Table 4).

In general, the 3D response surface plot is a graphical representation of the regression equation for the optimization of the reaction variables. Figure 1(a-f) described the 3D surfaces linked to the effect of two variables on the yield of HSME (biodiesel). The curvatures nature of 3D surfaces in Fig. 1b, c and f indicated the mutual interaction of the reaction time with reaction temperature, methanol/oil molar ratio with reaction temperature and methanol/oil molar ratio with reaction time, respectively. Meanwhile, there was a moderate interaction examined between methanol/oil molar ratio with catalyst amount and catalyst amount with reaction temperature, (Fig.1a and e), but no interaction was observed between reaction time and catalyst amount as represented in Fig.1d. The optimal condition predicted by the model were

methanol/oil molar ratio 6.21, catalyst amount 1.03 (%wt.), reaction temperature 51 ^{o}C, and reaction time 63 min, which gave 99.71% (w/w). Using these optimal condition values for three independent experimental replicates, an average HSME yield of 99.23% (w/w) was achieved, which was within the range predicted by the model.

3.3 *Quality and fuel properties of HSME*

Table 5 shows the properties of the HSME in comparison with ASTM biodiesel and DIN EN 14214 standards. All the tested characteristics and fuel properties of the HSME satisfied both the ASTM D 6751 and DIN EN 1424 standards. Gas chromatography analysis of fatty acids present in the HSME is shown in Table 6. The results indicated HSME was highly unsaturated. The dominant fatty acids were oleic (58.34%), arachidic (1.55%), palmitic (18.28%) and linoleic (21.19%).The total unsaturated fatty acid composition of the HSME was 79.53%.

3.4 *Engine Performance at Various Blends*

The performance characteristics of HSME and diesel blends are shown in Fig. 2(a-b). It was observed that from 20% up to 90% blends of HSME with AGO gives quite satisfactory performance related to CO and NO. The cetane number and viscosity of the blends lower than 10% or higher than 90% are not effective to give good performance.

4. Conclusions

In this study, experiments were conducted using RSM to determine the effects of four reaction factors namely methanol/oil molar ratio, reaction temperature, catalyst concentration and reaction time on HSME yield in the transesterification of the Sorrel seed oil. The maximum HSME conversion yield was validated as 99.23% (w/w) at the reaction temperature of 63 ^{o}C, a catalyst amount of 1.03 wt. %, methanol/oil molar ratio of 6.21 and reaction time of 51 min. The fuel properties of the HSME were within the ASTM D6751 and DIN EN 14214 specifications. Emission assessment revealed 70% reduction of CO at B80, 80% reduction of NO concentration at B40.

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Table 1: Factors and Their Levels for Composite Central Design

Variable	Symbol	Coded factor levels				
		-2	-1	0	1	2
Reaction temperature (^oC)	X_1	50	55	60	65	70
Catalyst amount (wt %)	X_2	0.7	0.8	0.9	1.0	1.1
Reaction time (min)	X_3	40	45	50	55	60
Methanol/oil ratio	X_4	4	5	6	7	8

Table 2: Central Composite Design, Experimental, Predicted and Residual Values for Five – Level-Four Factors Response Surface Analysis

Std order	X_1 (^oC)	X_2 (wt %)	X_3 (min)	X_4	Experimental value (w/w %)	Predicted value (w/w %)	Residual values (w/w%)
1	-1	-1	-1	-1	89.30	89.35	-0.050
2	1	-1	-1	-1	90.00	89.79	0.210
3	-1	1	-1	-1	93.92	93.87	0.050
4	1	1	-1	-1	94.79	94.86	-0.066
5	-1	-1	1	-1	90.90	90.87	0.031
6	1	-1	1	-1	90.17	90.21	-0.039
7	-1	1	1	-1	93.67	93.57	0.096
8	1	1	1	-1	93.56	93.47	0.091
9	-1	-1	-1	1	86.99	86.88	0.110
10	1	-1	-1	1	90.70	90.78	-0.084
11	-1	1	-1	1	91.20	91.15	0.051
12	1	1	-1	1	95.78	95.61	0.170
13	-1	-1	1	1	90.73	90.65	0.077
14	1	-1	1	1	93.61	93.46	0.150
15	-1	1	1	1	93.10	93.11	-0.013
16	1	1	1	1	96.54	96.48	0.062
17	-2	0	0	0	90.15	90.22	-0.072
18	2	0	0	0	93.88	94.02	-0.140
19	0	-2	0	0	89.29	89.39	-0.097
20	0	2	0	0	96.80	96.92	-0.120
21	0	0	-2	0	90.64	90.73	-0.093
22	0	0	2	0	93.00	93.12	-0.120
23	0	0	0	-2	91.00	91.06	-0.058
24	0	0	0	2	91.44	91.60	-0.160
25	0	0	0	0	98.49	98.91	-0.420
26	0	0	0	0	99.30	98.91	0.390
27	0	0	0	0	99.10	98.91	0.190
28	0	0	0	0	98.65	98.91	-0.260
29	0	0	0	0	99.07	98.91	0.160
30	0	0	0	0	98.87	98.91	-0.043

Table 3a: Test of Significance for Every Regression Coefficient CCD

Source	Sum of Squares	df	Mean Square	F-Value	p-value
X_1	21.66	1	21.66	453.37	< 0.0001
X_2	85.05	1	85.05	1780.23	< 0.0001
X_3	8.54	1	8.54	178.84	< 0.0001
X_4	0.43	1	0.43	9.04	0.0088
X_1X_2	0.31	1	0.31	6.45	0.0227
X_1X_3	1.20	1	1.20	25.10	0.0002
X_1X_4	12.04	1	12.04	252.03	< 0.0001

X_2X_3	3.28	1	3.28	68.57	< 0.0001
X_2X_4	0.060	1	0.060	1.26	0.2800
X_3X_4	5.09	1	5.09	106.44	< 0.0001
X_1^2	79.07	1	79.07	1655.12	< 0.0001
X_2^2	56.91	1	56.91	1191.17	< 0.0001
X_3^2	83.68	1	83.68	1751.53	< 0.0001
X_4^2	98.67	1	98.67	2065.28	< 0.0001

Table 3b: Analysis of Variance of Regression Equation

Source	Sum of squares	df	Mean Square	F-value	p-value
Model	361.87	14	25.85	541.03	< 0.0001
Residual	0.72	15	0.048		
Lack of Fit	0.26	10	0.026	0.28	0.9589
Pure Error	0.46	5	0.092		
Cor Total	362.59	29			
			R-Sq = 99.40%,	R-Sq(adj) = 99.62%	

Table 4: ANOVA for Response Surface Quadratic Model for Intercept.

Factors	Coefficient Estimate	df	Standard Error	95%CI Low	95%CI High	VIF
Intercept	98.91	1	0.089	98.72	99.10	-
X_1	0.95	1	0.045	0.85	1.05	1.00
X_2	1.88	1	0.045	1.79	1.98	1.00
X_3	0.60	1	0.045	0.50	0.69	1.00
X_4	0.13	1	0.045	0.039	0.23	1.00
X_1X_2	0.14	1	0.055	0.022	0.26	1.00
X_1X_3	-0.27	1	0.055	-0.39	-0.16	1.00
X_1X_4	0.87	1	0.055	0.75	0.98	1.00
X_2X_3	-0.061	1	0.055	-0.57	-0.34	1.00
X_2X_4	0.56	1	0.055	-0.18	0.55	1.00
X_3X_4	-1.70	1	0.055	0.45	0.68	1.00
X_1^2	-1.44	1	0.042	-1.79	-1.61	1.05
X_2^2	1.75	1	0.042	-1.53	-1.35	1.05
X_3^2	-1.90	1	0.042	-1.84	-1.66	1.05
X_4^2	98.67	1	0.042	-1.99	-1.81	1.05

Table 5: Properties of HSME in Comparison with Biodiesel Standards

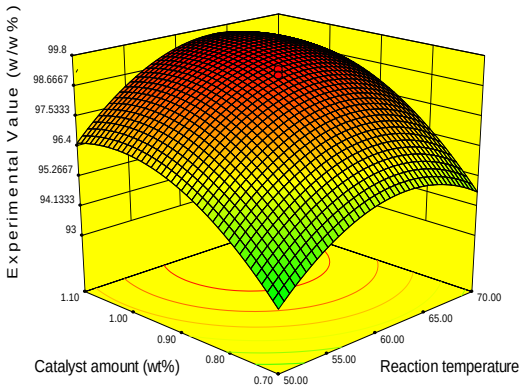
Parameters	HSME	ASTM D6751	DIN EN 14214
Moisture content %	<<<1ppm	< 0.03	0.02
Specific gravity@15 ^oC	0.882	0.86-0.90	0.85
Viscosity at 40 ^oC (cP)	5.80	1.9-6.0	3.5-5.0
Iodine Value (g I_2/100g)	64.47	-	120 max
Acid Value	0.24	< 0.80	0.5 max
Density (kg/m^3) at 25 ^oC	0.92	0.84	0.86-0.90
Saponification value (mg KOH/g oil)	148.49	-	-
Higher heating value (MJ/kg)	42.48	-	-
Diesel index	81.94	50.40	-
API	32.65	36.95	-
Cetane number	69.0	47 min	51 min
Aniline point	250.96	331.00	-

Pour Point ^{o}C	-15	Not specific	Not specific.
Cloud Point ^{o}C	+5	Report	Not specific.
Flash Point ^{o}C	186	93 min	120 min

Table 6: Fatty Acids Compositions of the HSME Produced

Fatty acid	Compositions %
Palmitic acid (C16:0)	18.280
Palmitoleic acids (C16:1)	0.055
Stearic acids (C18:0)	0.213
Oleic acids (C18:1)	58.337
Linoleic acids (C18:2)	21.194
Linolenic acid (C18:3)	0.165
Myristic acid (C14:0)	0.0943
Arachidonic acid (C20:4)	1.548
Other	0.114
Total	100

(a)



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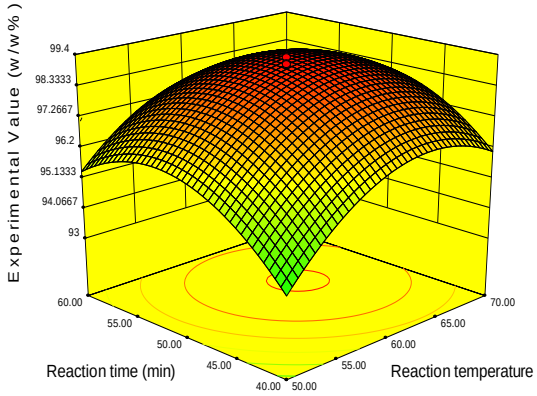

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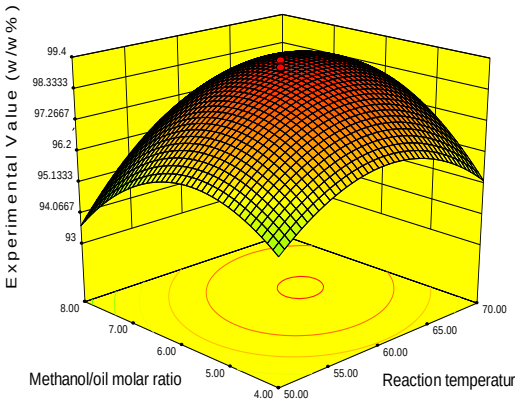

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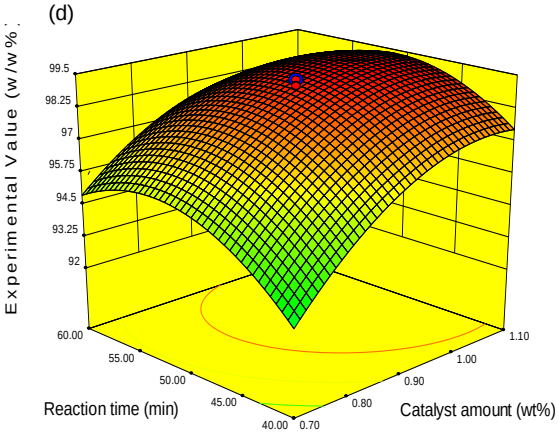

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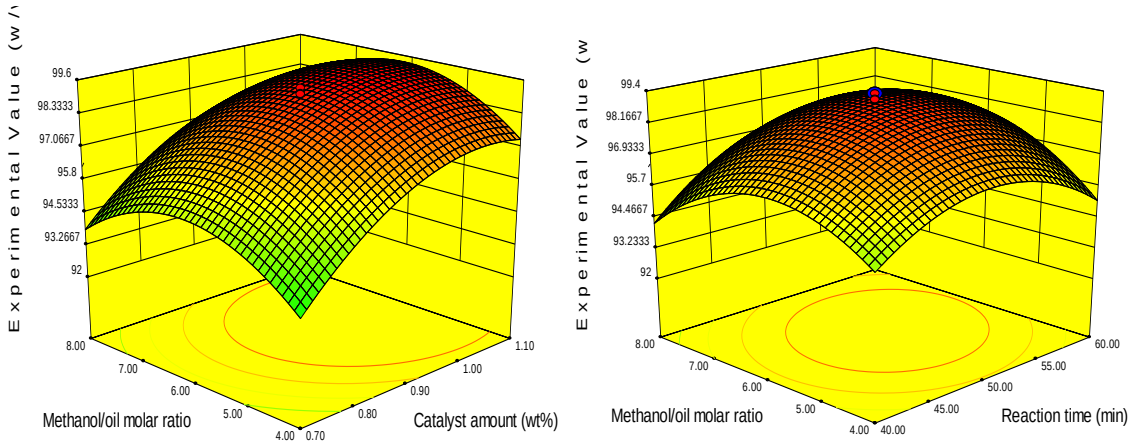
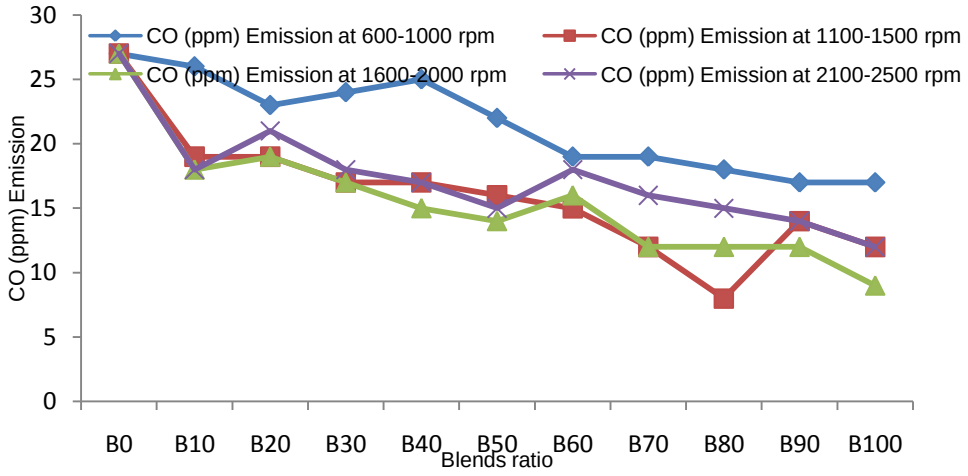


Figure 1: Response surface plots for HSME production

(a)



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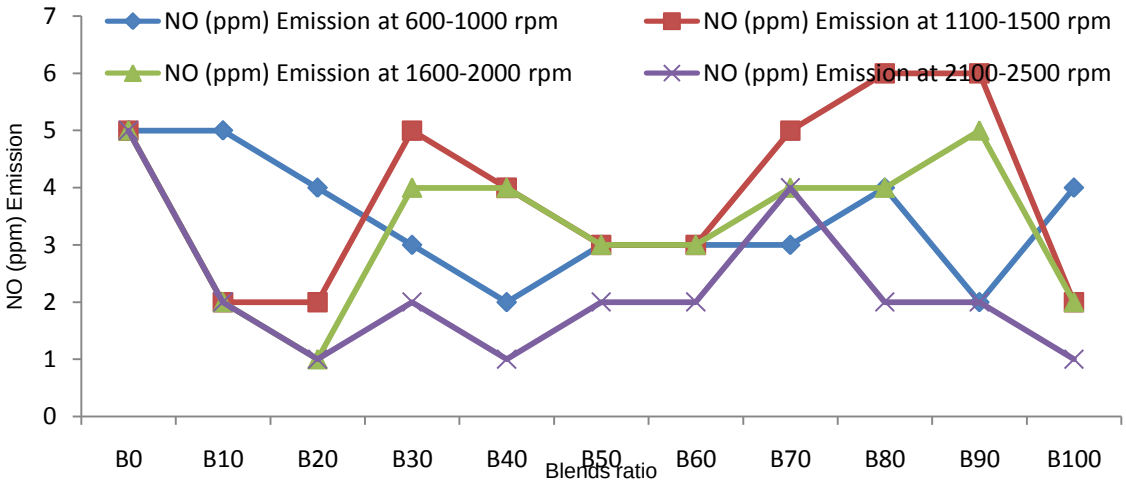

Figure 2 : Plots of performance characteristics of HSME and diesel blends