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ACID-CATALYZED PRETREATMENT OF *HEVEA BRASILIENSIS* (RUBBER) OIL VIA ESTERIFICATION PROCESS: MODELING AND OPTIMIZATION STUDIES

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ABSTRACT

The present study investigated modelling and optimization of acid esterification of non-edible *Hevea brasiliensis* (rubber) oil towards reduction of its very high free fatty acid (FFA) content (22.2 ± 0.03%) using response surface methodology (RSM). The process variables examined in the esterification reaction were methanol-to-oil molar ratio (15:1 – 30:1), H_2SO_4 concentration (1 – 2 wt.%), reaction temperature (55 – 65 °C) and reaction time (1 – 2 h) by central composite design (CCD). A second-order polynomial model was developed to assess significant synergistic impact among the process variables on the FFA content of the oil. Methanol-to-oil molar ratio had the most significant impact of the process variables. Optimal condition for the FFA reduction was achieved as methanol-to-oil molar ratio of 25.74, H_2SO_4 concentration of 2.00 wt.%, reaction temperature of 63.04 °C and reaction time of 1.51 h with predicted FFA content of 1.02%. Confirmatory test of the predicted optimal condition in the laboratory gave an average FFA content of 0.99 ± 0.021%, which corresponds to 95.5% conversion. Thus, the model obtained could be used for processes employed for the pretreatment of oils with high FFA content, which inhibits their conversion to biodiesel via transesterification process.

Keywords: *Hevea brasiliensis oil, free fatty acid, pretreatment, esterification, modelling, optimization, response surface methodology*

1. INTRODUCTION

The high price of biodiesel is the leading challenge to its market penetration and researchers in the present time have attempted several means to lower its high cost. Nearly 75% cost of biodiesel production is connected with the quality of its feedstock (Šánek et al., 2015) and approximately 95% of biodiesel is synthesized from edible oils such as sunflower, canola, soybean and rapeseed oils. However, utilization of edible oils could result into food shortage thereby creating possibility of instability between food and fuel market. Therefore, the utilization of inexpensive and readily available non-edible vegetable oils (VOs) as primary feedstock for synthesis of biodiesel is a plausible approach to reducing its total production cost. Hevea brasiliensis oil (HBO), also known as rubber oil, is a non-edible VO which contains 35 – 50 wt.% oil content (Onoji et al., 2016) and has been reported for its utilization as a feedstock for biodiesel synthesis (Dhawane et al., 2017; Onoji et al., 2017). It is noteworthy that the tropical atmosphere in Nigeria is good for rubber tree plantation and the recently released statistical analysis by FAO (2017) shows Nigeria has an estimated total production of 159,264 metric tonnes of natural rubber. Unfortunately, HBO from Nigeria contains high free fatty acid (FFA) content, hence, it cannot be used for direct transesterification into biodiesel.

Transesterification process is a widely accepted way of synthesizing biodiesel which involves the reaction of VO with an alcohol over an alkali catalyst. High FFA is the primary problem against direct conversion of VO into alkyl esters. This is because FFA reacts with alkali to form soap leading to reduction in biodiesel yield (Chai et al., 2014). Moreover, the soap can gel, thus, hindering separation and purification of the products i.e. glycerol and esters (Demirbaş, 2003). Hence, acid-catalysed pretreatment of VO with high FFA prior to alkaline-catalysed transesterification has been suggested (Ramadhas et al., 2005; Ishola et al., 2017).

Esterification process is a reversible reaction between an organic acid (FFA) and alcohol (e.g. methanol) for lowering the FFA level in oils in the presence of a catalyst (e.g. H_2SO_4). The process converts the FFA present in oils to alkyl esters (Farobie and Matsumura, 2015). Esterification reaction hinges on several variables such as FFA content, catalyst amount, molar ratio of MeOH-to-oil, temperature of reaction and reaction time (Javidialesaadi and Raeissi, 2013). In literature, FFA of castor oil was lowered from 4.04 to 1.08% via esterification with 1% w/w H_2SO_4 as catalyst under temperature of 50 ° C and MeOH-to-oil molar ratio of 15:1 under 2.09 h reaction time (Halder et al., 2015). Kostić et al. (2016) carried out esterification reaction of waste plum stones oil to reduce its acid number from 31.60 to 0.47 mg KOH/g oil under optimized condition of 2% H_2SO_4, 8.5:1 molar ratio of MeOH-to-oil, 45 °C reaction temperature and 60 min reaction time using central composite design (CCD) in RSM. Ishola et al. (2017) reported the optimization of palm kernel oil esterification in which the acid value was lowered from 22 to 1.54 mg KOH/g oil using 6 w/v of ferric sulphate as catalyst, 65 °C temperature, 25 min reaction time and 2:1 molar ratio of MeOH-to-oil of via the Box-Behnken design in RSM. However, very little information is found in literature (Ahmad et al., 2014) on the optimization of pretreatment process of high FFA rubber oil via RSM. Hence, establishing optimum operating conditions for HBO pretreatment needs to be addressed.

Therefore, the main goal of this investigation is to model and optimize the acid-catalysed pretreatment process for the reduction of the high FFA content of HBO. Modelling of the pretreatment process was performed by CCD to investigate the influence of the process variables (MeOH-to-oil molar ratio, H_2SO_4 amount, reaction temperature and reaction time) on the FFA of HBO. In order to minimize the acid FFA of the HBO, the process variables were optimized using RSM.

2. MATERIALS AND METHODS

2.1. Materials, Chemicals and Reagents

The HBO employed in the investigation was commercially sourced from the Rubber Research Institute of Nigeria, Iyanomo, Edo State, Nigeria. All reagents used were as previously reported by Betiku et al. (2016) and used without further purification. The quality of the HBO used was analyzed by the testing procedures previously described by Betiku et al. (2014). Characterization such as acid value, kinematic viscosity, iodine value and saponification value were carried out in the laboratory.

2.2. Major Design Considerations

The fractional factorial (four-factor-three-level) of CCD was chosen for this study which produced 21 experimental conditions. These comprised of 16 non-centre and 5 centre points to show the internal attributes pertaining to the process region and were thereafter carried out in the laboratory. Table 1 depicts the level of each process variable in the study.

Table 1: Process variables and their levels based on CCD

Variable	Units	Symbol	Level	
			Low	High
MeOH:HBO molar ratio	-	A	15	30
Catalyst amount	wt.%	B	1	2
Reaction temperature	°C	C	55	65
Reaction time	h	D	1	2

Multiple regression was applied to fit the coefficients of the mathematical model of the responses. Quality of fit of the model was checked employing the test of significance and ANOVA. Response variable (%FFA content) was fitted by a second-order mathematical model in order to correspond it with the process variables. Equation (1) explains the general expression for a second-order mathematical model. Design-Expert version 10.0 (Stat-Ease Inc., Minneapolis, MN, USA) was applied for all the analyses.

$$Y = \zeta_o + \sum_{p=1}^{4} \zeta_p X_p + \sum_{p=1}^{4} \zeta_{pp} X_p^2 + \sum_{p<q}^{4} \zeta_{pq} X_p X_q + \lambda \qquad (1)$$

where, Y is predicted response (%FFA content) after pretreatment, ζ_o is the intercept value, ζ_p (p = 1, 2, ..., n) is the linear coefficient , ζ_{pp} is the second order coefficient, ζ_{pq} is the coupling coefficient and λ is the random error component

2.3. Acid-catalysed Esterification Reaction of HBO

A known volume of the HBO was charged into a batch reactor system of 250-ml (2-necks) round bottom flask attached with a condensing system and was positioned on a temperature controlled magnetic stirrer with hot plate. Specific volume of alcohol (methanol) was introduced to the HBO and was stirred for 5 min (Betiku et al., 2016). Then, a measured amount of H_2SO_4-catalyst was introduced to the HBO-methanol mixture in the reactor. The experiments were conducted according to the specification of each process condition generated in the design matrix. At the end of each experiment, the resulting mixture was promptly channelled into a separating funnel and left to stand for 2 h. After the formation of distinct interphase, the lower layer containing the esterified oil was discharged into a beaker and traces of methanol left inside was removed by heating it off before the determination of its acid value. Acid value and %FFA content of the pretreated HBO were calculated using Equations (2) and (3).

$$\text{Acid value (mg KOH/g oil)} = \frac{V \times N \times 56.1}{W_{HBO}} \times 100 \qquad (2)$$

where, V represents titrated value, N represents normality of KOH solution, WHBO represents weight of the HBO sample utilized and 56.1 represents the molecular mass of KOH in g/mol.

$$\text{\%FFA content } (as\ oleic) = \frac{\text{Acid value}}{1.99} \qquad (3)$$

2.4. Statistical Check of the Developed Model

The efficacy of the model developed was assessed by some statistical criteria such as coefficient of determination (R2), adjusted R2, standard deviation (S.D.) and adequate precision. The statistical criteria were computed using Equations (4) – (7).

$$R^2 = 1 - \frac{SS_{residual}}{SS_{model} + SS_{residual}} \qquad (4)$$

$$\text{Adjusted } R^2 = 1 - \frac{SS_{residual}/DF_{residual}}{(SS_{model} + SS_{residual})/(DF_{model} + DF_{residual})} \qquad (5)$$

$$S.D. = \sqrt{MS_e} \qquad (6)$$

$$\text{Adequate precision} = \frac{max(\text{Y}) - min(\text{Y})}{\sqrt{\frac{p\sigma^2}{n}}} \qquad (7)$$

where, in Equations (4) - (7), SS is the sum of squares, DF is the degree of freedom, S.D. is the standard deviation, MSe is the residual mean square, Y is the predicted response, p is the number of model variables, σ 2 is the residual mean square from ANOVA table and n is the number of experimental runs.

2.5. Optimization of HBO Pretreatment Process

For optimum reduction of %FFA content of HBO to be achieved, optimization of the examined operating variables (molar ratio of MeOH-to-HBO, catalyst amount, reaction temperature and reaction time) was done with the aid of the in-built optimization algorithm of the Design-Expert software. This was performed by setting the %FFA at minimum, while the operating variables were fixed within the ranges examined. The predicted optimum condition was thereafter confirmed by performing experiment in triplicate in the laboratory. Design-Expert software was applied to obtain the optimum set of process condition.

3. RESULTS AND DISCUSSION

3.1. Physicochemical Properties of HBO

The physicochemical properties of the unrefined HBO employed in the study are shown in Table 2.

Table 2: Physicochemical properties of HBO used in this study

Property (unit)	Value
Acid value (mg KOH/g oil)	44.1
FFA (%) (as oleic)	22.2
Kinematic viscosity (mm^2/s)	71.9
Iodine value (g I_2/100 g oil)	122.6
Saponification value (mg KOH/g oil)	180.7

The acid value and FFA content were high making the HBO unsuitable for biodiesel synthesis by direct base-catalysed transesterification. Hence, acid-catalysed pretreatment of the HBO is necessary to reduce the acid value and FFA content. HBO has been reported with high acid value and %FFA content (Ramadhas et al., 2005; Onoji et al., 2017).

3.2. Developed Model Equation and ANOVA

The CCD design matrix, the experimental and the predicted data of the H_2SO_4-catalyzed pretreatment of HBO via esterification reaction are depicted in Table 3. From the results, FFA level of the HBO varied from 1.46 to 5.83%. A quadratic mathematical model was selected as the best fit model for analysing the obtained experimental data. The mathematical model was fitted to the experimental data for statistical analysis by ANOVA. Table 4a illustrates the ANOVA for the second-order model.

Table 3: Experimental design matrix with corresponding observed and predicted data

	Coded values of process variables				FFA (%)	
Run no.	A	B (wt.%)	C (°C)	D (h)	Experimental	Predicted
1	1	1	1	-1	1.9074	1.91
2	0	0	-1.682	0	3.927	3.46
3	1	-1	1	1	1.4586	1.74
4	0	0	0	0	2.244	2.50
5	-1	-1	-1	-1	4.6002	4.63
6	1	-1	-1	1	2.8723	2.89
7	1.682	0	0	0	2.0196	1.87
8	-1.682	0	0	0	5.8344	5.68
9	0	1.682	0	0	1.7952	1.32
10	0	0	0	1.682	2.144	1.96
11	1	1	-1	-1	2.9172	3.06
12	0	0	0	0	2.244	2.50
13	0	0	0	0	2.244	2.50
14	0	0	0	0	2.4684	2.50
15	0	-1.682	0	0	4.1514	3.67
16	0	0	1.682	0	1.5708	1.53
17	0	0	0	0	2.1991	2.50
18	-1	1	-1	1	2.9172	3.53
19	-1	1	1	1	2.6928	2.38
20	-1	-1	1	-1	3.366	3.48
21	0	0	0	-1.682	3.0296	3.03

Table 4a: ANOVA for the full quadratic model

Source of variation	SS	DF	MS	*F*-value	*p*-value
Model	22.64	14	1.62	10.46	0.0043
A-MeOH:HBO molar ratio	7.28	1	7.28	47.09	0.0005
B-Catalyst amount	2.78	1	2.78	17.96	0.0055
C-Reaction temperature	4.51	1	4.51	29.16	0.0017
D-Reaction time	0.39	1	0.39	2.54	0.1623
AB	0.029	1	0.029	0.19	0.6819
AC	0.12	1	0.12	0.75	0.4188
AD	0.72	1	0.72	4.69	0.0735
BC	0.25	1	0.25	1.62	0.2506
BD	1.12	1	1.12	7.25	0.0359
CD	0.046	1	0.046	0.30	0.6054
A^2	3.21	1	3.21	20.78	0.0039
B^2	0.24	1	0.24	1.54	0.2604
C^2	0.033	1	0.033	0.21	0.6602
D^2	0.001587	1	0.001587	0.010	0.9226
Residual	0.93	6	0.15		
Lack of Fit	0.88	2	0.44	34.53	0.0030
Pure Error	0.051	4	0.013		
Corrected Total SS	23.57	20			

SS – Sum of squares, DF – degree of freedom, MS – mean square

Table 4b: ANOVA for the reduced model

Source of variation	SS	DF	MS	F-value	*p*-value
Model	21.90	7	3.13	25.25	< 0.0001
A-MeOH:HBO molar ratio	7.28	1	7.28	58.72	< 0.0001
B-Catalyst amount	2.78	1	2.78	22.40	0.0004
C-Reaction temperature	4.51	1	4.51	36.36	< 0.0001
D-Reaction time	1.38	1	1.38	11.13	0.0054
AD	0.72	1	0.72	5.85	0.0310
BD	1.12	1	1.12	9.04	0.0101
A^2	3.09	1	3.09	24.93	0.0002
Residual	1.61	13	0.12		
Lack of Fit	1.57	9	0.17	15.15	0.0094
Pure Error	0.046	4	0.011		
Corrected Total SS	23.51	20			

SS – Sum of squares, DF – degree of freedom, MS – mean square

However, the terms A, B, C, BD and A2 are the significant model terms (p-values <0.05). Since the model has several insignificant terms (p-value >0.05), model reduction may enhance the developed model by allowing for easy establishment in interpreting the contour and surface plots (Vázquez et al., 2009). In this case, D, AB, AC, AD, BC, CD, B2, C2 and D2 were insignificant. A reduced model was obtained by removing the insignificant terms, thereby accessing a dynamic model that can be used in subsequent investigations (Table 4b).

The results for the reduced model gave a quadratic regression relation which connects the response to the process variables as a function of the real values. The expression is as shown in Equation (8).

$$Y = 10.47236 - 0.32582A + 2.08835B - 0.11488C + 5.66002D - 0.12472AD - 2.32624BD + 0.00803715A^2 \tag{8}$$

where, Y is the %FFA content, A is MeOH-to-HBO molar ratio, B is the H_2SO_4 amount (wt.%), C is the reaction temperature (°C) and D is the reaction time (h).

The reduced quadratic model was subjected to ANOVA check to evaluate its performance (Table 4b). At 95% confidence level, the F-value and p-value of the model were 25.25 and <0.0001, respectively, indicating its significance. The results also showed that all the model terms relationships (linear, interactive and quadratic terms) of the operating variables are all significant, i.e. $p < 0.05$. Among all the significant terms, the linear term of MeOH-to-HBO molar ratio (A) had the greatest impact which was confirmed with its highest F-value (58.72) followed by the linear term of reaction temperature (C), then the quadratic term of MeOH-to-HBO molar ratio (A2), followed by the linear term of H_2SO_4 concentration (B), then the linear term of reaction time (D), followed by the coupling influence between H_2SO_4 concentration and reaction time (BD) and lastly, the coupling influence between MeOH-to-HBO molar ratio and reaction time (AD).

The quality of fit of the second-order model for the entire operation was computed and compared with the full quadratic model in Table 5.

Table 5: Comparison of statistical indicators of the developed quadratic model

Parameter	Full model	Reduced model
	Value	Value
R^2	0.9607	0.9315
Adjusted R^2	0.8688	0.8946
Standard Deviation	±0.39	±0.35
Signal to noise ratio (SNR)	12.23	20.09

The high R2 of 0.9315 obtained for the reduced model was slightly lower than 0.9607 estimated for the full model of Equation (3). Thus, it shows that 93.15% variation of the reduced second-order model could be explained in the %FFA content as described by the regression equation. However, the previous value of 0.8688 obtained for the adjusted R2 was improved with increase in value to 0.8946, which strengthened the significance of the reduced model. Statistical significance of the model was reaffirmed with a lower value of S.D. (0.35) compared to the value of 0.39 evaluated for the experimental data of the full model. This indicates that the reduced model produced a satisfactory correlation between the predicted and the experimental responses. Moreover, another improvement was that the SNR value of 20.09 estimated for the reduced model was higher in comparsion with the value of 12.23 evaluated for the full model, thereby, pointing to sufficient signal in predicting the response of the reduced model. Adequate precision determines the ratio of signal-to-noise. It has earlier been reported that SNR value greater than 4 is desirable (Anderson and Whitcomb, 2016). The plot of the predicted %FFA content against the experimental %FFA content is shown in Fig. 1. It can be noticed from the plot that the fitted points lie very close to the diagonal line, suggesting that the model developed was adequate and the assumptions for the ANOVA were not violated.

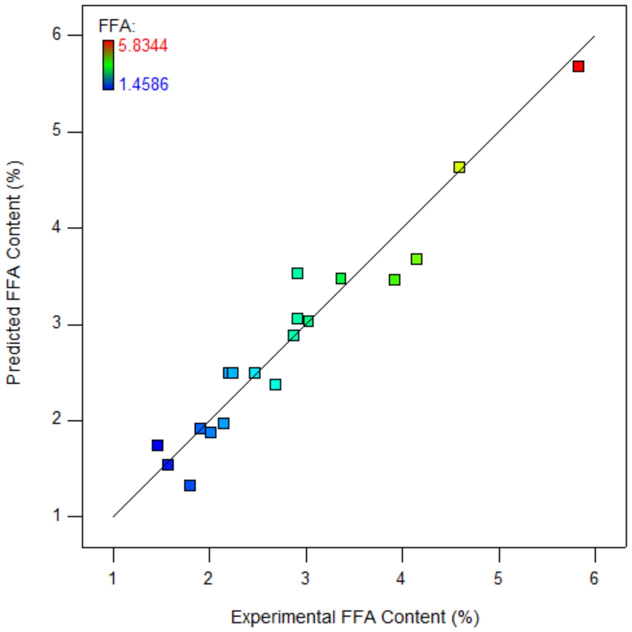

Fig. 1: Plot of predicted vs. experimental FFA content.

3.3. Model Sufficiency Check

The sufficiency of the developed model was checked through the plots displayed in Fig. 2 (a and b). Fig. 2a illustrates the normal probability plot of residuals. It could be observed that the residuals plot closely to the straight line demonstrating that the normality hypothesis is not violated. Fig. 2b depicts the plot of residuals against predicted response.

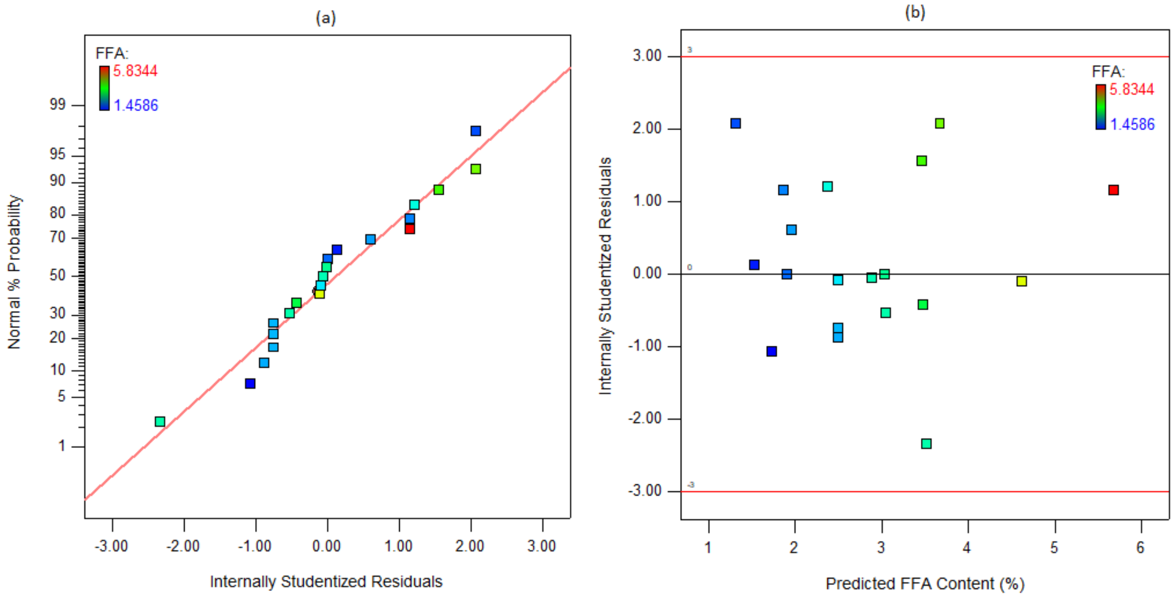

Fig. 2: Model sufficiency plots

From the plot, it can be seen that the residuals disperse at random, illustrating that the deviation of the real observations is the same for all the experimental data.

3.4. Interactive Impacts of Process Variables

Contour plots for the reduced model of the esterification process on the FFA content of HBO are as displayed in Fig. 3 (a and b). Fig. 3a illustrates the contour plot of FFA content based on the synergy between reaction time and MeOH:HBO molar ratio. It can be observed from the plot that the lowest FFA reduction was established when the molar ratio of MeOH:HBO and reaction time were both at their maximum chosen level, at a constant H_2SO_4 concentration of 1.5 wt.% and reaction temperature of 60 °C. Fig. 3b shows the contour plot for the relationship between reaction time and H_2SO_4 amount with respect to the FFA content. The plot reveals that increase in both reaction time and H_2SO_4 concentration reduces FFA content. The lowest FFA level was reached at the maximum reaction time and at the maximum H_2SO_4 concentration, provided the MeOH:HBO molar ratio and reaction temperature are maintained at 22.5 and 60 °C, respectively.

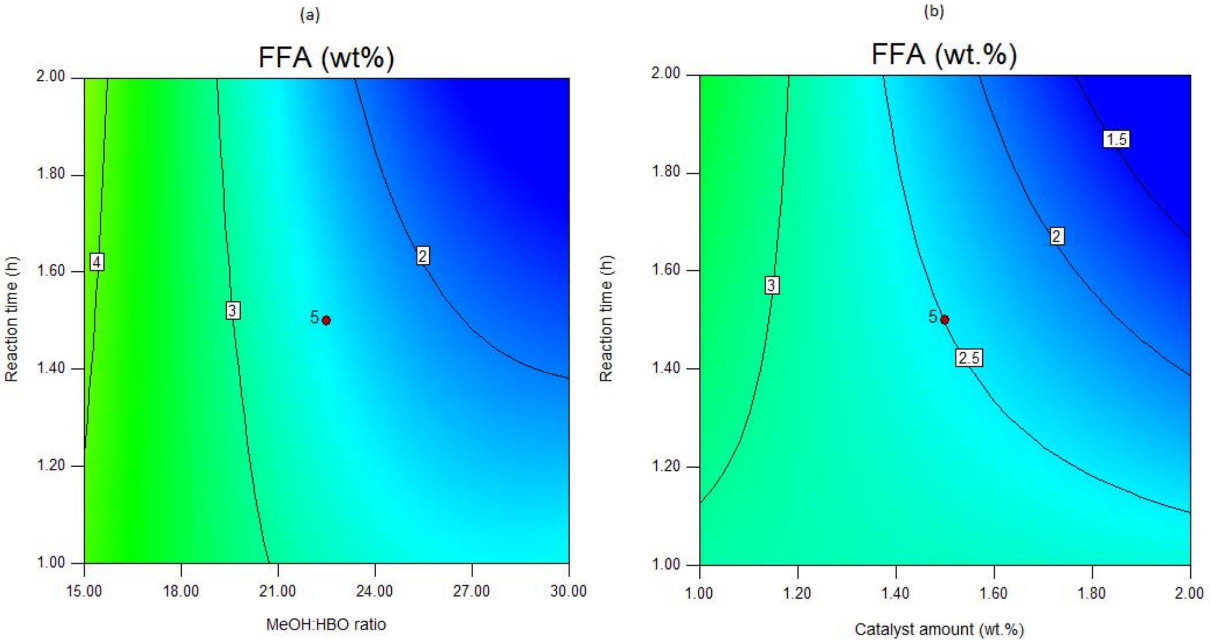

Fig. 3: Contour plots for FFA reduction in HBO

3.5 Optimization of Process Variables

For the process variables optimization, the in-built optimization algorithm of RSM was applied. The predicted optimal condition established for the FFA reduction in HBO acid-catalysed esterification process was MeOH-to-HBO molar ratio of 25.74, H_2SO_4 concentration of 2.00 wt.% and reaction time of 1.51 h with predicted FFA content of 1.02%. The predicted optimal condition was verified by performing three separate experimental replicates and the average FFA content of HBO was estimated for the process was estimated to be 0.99%. With a 95.5% reduction, this established that the model developed adequately described the esterification process under investigation.

4. CONCLUSIONS

Optimization studies for FFA content reduction in the HBO were performed by applying fractional factorial (four-factor-three-level) CCD in RSM to obtain optimized process condition for the acid-catalysed pretreatment. The FFA level was reduced from 22.2 to 1.02% according to the reaction that was carried out using 2.00 wt.% H_2SO_4 amount and 25.74 MeOH-to-HBO molar ratio at a reaction temperature of 63.04 °C for 1.51 h. Process variables influence on the reduction of FFA in the HBO were investigated. ANOVA of the reduced second-order model showed that all the terms are significant. Optimal condition established for the esterification process of HBO in this study can be used for cost-effective biodiesel production.

ABBREVIATIONS

ANOVA	analysis of variance
CCD	central composite design
FFA	free fatty acid
HBO	*Hevea brasiliensis* oil
MeOH	methanol
RSM	response surface methodology
R^2	coefficient of determination
S.D.	standard deviation
SNR	signal-to-noise ratio
VO	vegetable oil

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