

Acid-Catalyzed Esterification Pretreatment of High Free Fatty Acid Crude Rice Bran Oil for Biodiesel Production

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ABSTRACT

This study investigated the acid-catalyzed esterification of two brands of crude rice bran oil (CRBO) with free fatty acids (FFAs) content of about 8 and 10%, respectively. Experimental variables included reaction time, methanol-to-FFA molar ratio and sulfuric acid content with temperature and stirring speed fixed at 60 °C and 600 RPM, respectively. A central composite design was used initially for sequential experimentation and followed by a Box-Behnken design to refine the optimum process conditions. Results showed that final FFA in CRBO could be reduced to less than 1% FFA in a single-step. The methanol-to-FFA molar ratio had the maximum influence on the esterification process and was followed by the reaction time and amount of catalyst. The optimum conditions for FFA conversion in CRBO were: reaction time 90 and 48 min, 62:1 and 70:1 methanol-to-FFA molar ratio, 22.5 and 20% (w/w) sulfuric acid based on FFA for Brand I and II, respectively. Under these pretreatment conditions, initial FFA was reduced to 0.61 and 0.70%, respectively making the CRBO suitable for biodiesel production.

1. INTRODUCTION

The consumption of petroleum based fossil fuels keeps on rising with increasing industrialization all over the world. Concern about the inevitable depletion of fossil fuels has led to an extensive search for alternative fuels that are renewable and environmentally friendly. Biodiesel offers an attractive alternative to petroleum-based fuels and can be produced from a variety of feedstocks such as vegetable oils, animal fats, and waste cooking oil. Biodiesel is biodegradable and non-toxic, and easily blended with petroleum diesel for use in conventional unmodified engines (Mahmudul et al., 2017). Biodiesel is also known for minimizing environmental pollution due to the reduction in exhaust emission and toxic elements (Chen et al., 2018). However, perceived benefits of biodiesel production and use need to be critically analyzed prior to its economic feasibility and commercialization (Amin et al., 2017; Hanif et al., 2018).

The widespread use of biodiesel is mainly limited by its high production cost compared to

petroleum-based diesel and current state of the technology to process a wide variety of feedstocks (Baskar et al., 2016; Demirbas et al., 2016; Hanif et al., 2018; Grebemariam and Marchetti, 2017; Aransiola et al., 2014; Tabatabaei et al., 2015). A reduction in production cost can be achieved through the utilization of inexpensive, low quality feedstocks (Berchmans and Hirata, 2008; Atadashi et al., 2012). However, the presence of high free fatty acids (FFAs) in low quality feedstocks hinders the transesterification process necessitating a pretreatment step to convert FFA in feedstock to alkyl esters (FAME) by esterification reaction. Therefore, a two-step esterification-transesterification method is often used due to its moderate operating conditions, higher reaction rates and lower cost (Canakci and Van Gerpen, 2001; Ghadge and Raheman, 2005; Wang et al., 2006; Bouaid et al., 2012). A distinct advantage of acid-catalyzed esterification step is direct conversion of high FFA content into alkyl esters or biodiesel and thus reducing FFA content to an acceptable level for the subsequent transesterification step (Berchmans

and Hirata, 2008; Mohandass et al., 2016; Gunawardena et al., 2017).

Various process variables such as temperature, catalyst concentration, amount of methanol, reaction time and agitation are routinely optimized for maximizing FAME yield (Lin et al., 2009; Verma and Sharma, 2016). The application of design of experiment (DOE) and response surface methodology (RSM) for process optimization has been reported in a limited number of studies mainly for the transesterification process (Liao and Chung, 2011; Kamath et al., 2011). The DOE and RSM can estimate the effects of individual process variables as well as their interactions leading to the determination of more realistic optimum conditions (Natthapon and Krit, 2015).

Crude rice bran oil (CRBO) is available in large quantities in Asia Pacific region with a huge potential for biodiesel production (Allen Jeffery et al., 2017; Chhabra et al., 2017). However, CRBO remains an underutilized non-edible resource due to rapid spoilage of rice bran by lipase enzymatic action resulting in very high levels of FFAs. Thus, CRBO with high FFA requires acid-catalyzed pretreatment similar to other non-edible oil feedstocks to reduce the final FFA content $\leq 1\%$ suitable for alkali-catalyzed transesterification reaction (Sivakumar et al., 2013; Montefrio et al., 2010). The suitability of enzymatic treatment for the reduction of high FFA in CRBO has been reported in some studies (Wang et al., 2017; Li et al., 2018). However, acid-catalyzed methanolic esterification of CRBO with high FFA has been widely reported in several studies for biodiesel production (Zullaikah et al., 2005; Lin et al., 2009; Amin et al., 2012; Kattimani et al., 2014; Arora et al., 2016).

Many studies have reported optimum conditions for acid-catalyzed esterification for high FFA feedstocks determined by one-factor-at-a-time approach (Hamze et al., 2015; Farag et al., 2011). However, there are no published studies on the optimization of esterification process of CRBO using DOE and RSM to reduce the FFA in a single-step. The main purpose of this study was to determine the optimum process conditions such as reaction time, methanol-to-FFA molar ratio and the amount of catalyst for the esterification of two brands of CRBO with high FFA content. The approach based on DOE helps identify the relative contributions of the variables in the esterification process with minimum

experimentation and cost. Initially, a central composite design (CCD) was used for sequential experimentation and followed by Box-Behnken design (BBD) to develop models for determining the optimal process conditions.

2. METHODOLOGY

2.1 Materials

Two brands of CRBO with FFA content of approximately 8 and 10% (w/w) were obtained from Kasisuri Co., Ltd. and King Rice Bran Oil Company, and designated as Brand I and II, respectively. The reactant solutions used in esterification process consisted of methanol (laboratory grade, 95%) and sulfuric acid (laboratory grade, 98%) as the catalyst. Potassium hydroxide (laboratory grade, 85%) was used for preparing standard solution to measure the FFA content of oil samples. Hydrochloric acid (laboratory grade, 37%) was used as a standard solution for KOH. The CRBO samples used in these experiments were of brownish yellow color.

2.2 Esterification

Esterification was carried out in a single-step process with sulfuric acid as homogenous catalyst. The samples weighing 50 g were placed in a conical flask and heated to 60 °C by using a hot plate with magnetic stirrer. A mixture of sulfuric acid and methanol was poured into the heated flask containing oil. The amounts of sulfuric acid (g) and methanol (g) were calculated based on the % FFA content in oil sample and molar ratio of methanol to FFA, respectively. The agitation speed was fixed at 600 revolutions per minute (RPM) for thorough mixing of methanol and oil. The reaction was allowed to proceed at 60 °C for different times based on the experimental design.

Reaction time, molar ratio of methanol-to-FFA and sulfuric acid as catalyst were used as independent variables. Theoretically, one mole of methanol is needed to react with one mole of FFA. However, an excess amount of alcohol is used to prevent the reversible reaction. At the end of reaction, the oil mixture was allowed to settle down in a separating funnel. The separated sample was washed with distilled water slowly to reduce the pH level to neutral and remove the impurities. Subsequently, the sample was dried in an oven at 100 °C to remove the residual water prior to acid value measurement.

2.3 Analysis of FFA

The FFA present in an oil sample was determined as the acid value (AV) by titrating the oil sample in a flask with 10 mL of 2-propanol against standard potassium hydroxide (KOH) solution with phenolphthalein as an indicator. The standard method for FFA titration in oil was followed (AOCS, 2017). The acid value (AV) is expressed as (mg KOH/g oil) as shown below.

$$AV = \frac{\text{Volume of KOH used (mL)} \times 56.1 \times N \text{ of KOH}}{\text{Weight of sample (g)}} \quad (1)$$

$$FFA (\%) = AV \times 0.503 \quad (2)$$

$$\text{Conversion of FFA (\%)} = \frac{\text{Initial FFA} - \text{Final FFA}}{\text{Initial FFA}} \times 100\% \quad (3)$$

The strength of KOH solution was standardized using diluted HCl solution.

$$\text{Normality of KOH} = \frac{\text{Volume of HCl used} \times N \text{ of HCl}}{\text{Volume of KOH used}} \quad (4)$$

A correction factor was obtained to adjust the normality of KOH solution in Equation 1.

2.4 Experimental design

The esterification of two brands of CRBO with different initial FFA content (% w/w) was carried out using DOE and RSM, respectively. A review of literature indicated that the esterification process of high FFA oils is most affected by the factors such as the reaction time, methanol-to-FFA molar ratio and amount of catalyst whereas the reaction temperature and stirring speed were usually fixed at 60 °C and 600 RPM, respectively (Arora et al., 2015; Chai et al., 2014). The respective ranges of these independent variables (reaction time, min (X_1), methanol: FFA (X_2), and amount of catalyst (% w/w FFA, X_3) for esterification process were selected based on the review of literature. (Lin et al., 2009; Zullaikah et al., 2005; Amin et al., 2012; Kattimani et al., 2014; Arora et al., 2015; Chai et al., 2014). Therefore, the effect of three independent variables on the conversion of initial FFA in CRBO was investigated. Initially, a five-level-three-factor central composite design (CCD) was used for sequential experimentation and followed by a Box-Behnken design (BBD) to further improve the models for predicting the final FFA in two brands of CRBO. The independent variables and their levels in coded and actual units are shown in Table 1.

Table 1. Independent variables used for CCD and BBD in esterification experiments.

Variables	CRBO Brand	CCD coded levels					BBD coded levels		
		-1.68	-1	0	1	1.68	-1	0	1
Time, min (X_1)	I	40.8	60	120	180	220.8	30	60	90
	II	40.8	60	120	180	220.8	30	60	90
Methanol:FFA (X_2)	I	14.8	25	40	55	65.2	30	60	90
	II	9.8	20	35	50	60.2	30	50	70
Catalyst (% w/w FFA, X_3)	I	11.6	15	20	25	28.4	5	15	25
	II	11.6	15	20	25	28.4	10	15	20

2.5 Statistical analysis

The following second-order polynomial model (Equation 5) was fitted to the experimental data obtained for the esterification of the both brands of CRBO using regression analysis in MS Excel.

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i \cdot X_i + \sum_{i=1}^3 \beta_{ii} \cdot X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} X_i X_j \quad (5)$$

Where Y is the response (final FFA, % w/w); β_0 is constant, β_i , β_{ii} , and β_{ij} are coefficients; x_i , x_j are the independent variables. Equation 5 was used for

developing the models based on CCD and BBD, and evaluating the effects of linear, interaction and quadratic terms in CCD. Subsequently, optimal conditions for esterification were determined by the Excel Solver function using the developed models.

3. RESULTS AND DISCUSSION

3.1 Models based on CCD and BBD

The CCD had eight factorial, six axial and six center point experiments resulting in a total of 20 experimental runs for each brand of CRBO as shown

in Table 2 and Table 4 based on the coded and actual conditions given in Table 1. A sequential approach was used to analyze the CCD model for evaluating the effects of individual factors and their interactions. In addition, the direction of steepest gradient for the reduction of FFA due to esterification was determined using the Solver function in Excel. Subsequently, the low and high values of independent variables in CCD were

adjusted and used in the BBD as shown in Table 1. Thus, it was possible to refine the optimum conditions subsequently based on the BBD. The BBD design had a total of 15 experimental runs for each brand of CRBO as shown in Table 3 and Table 5. The experimental and predicted values of final FFA in CRBO based on CCD and BBD are shown in Table 2 and Table 3 for Brand I and in Table 3 and Table 4 for Brand II, respectively.

Table 2. Final FFA (%) of CRBO Brand I after esterification based on CCD.

Run No.	X ₁ (Time, min)	X ₂ (MEOH:FFA)	X ₃ (% w/w FFA)	Brand I	
				Experimental	Predicted
1	-1 (60)	-1 (25)	-1 (15)	2.78	2.24
2	1 (180)	-1 (25)	-1 (15)	2.66	2.42
3	-1 (60)	1 (55)	-1 (15)	0.92	1.25
4	1 (180)	1 (55)	-1 (15)	1.94	1.36
5	-1 (60)	-1 (25)	1 (25)	1.54	1.84
6	1 (180)	-1 (25)	1 (25)	2.70	2.09
7	-1 (60)	1 (55)	1 (25)	1.10	1.06
8	1 (180)	1 (55)	1 (25)	0.98	1.24
9	-1.68 (40.8)	0 (40)	0 (20)	1.66	1.49
10	1.68 (220.8)	0 (40)	0 (20)	1.24	1.79
11	0 (120)	-1.68 (14.8)	0 (20)	2.06	2.56
12	0 (120)	1.68 (65.2)	0 (20)	1.14	1.02
13	0 (120)	0 (40)	-1.68 (11.6)	1.30	1.77
14	0 (120)	0 (40)	1.68 (28.4)	1.42	1.33
15	0 (120)	0 (40)	0 (20)	1.20	1.17
16	0 (120)	0 (40)	0 (20)	1.26	1.17
17	0 (120)	0 (40)	0 (20)	1.16	1.17
18	0 (120)	0 (40)	0 (20)	1.14	1.17
19	0 (120)	0 (40)	0 (20)	1.06	1.17
20	0 (120)	0 (40)	0 (20)	1.28	1.17

Table 3. Final FFA (%) of CRBO Brand I after esterification based on BBD.

Run No.	X ₁ (Time, min)	X ₂ (MEOH:FFA)	X ₃ (% w/w FFA)	Brand I	
				Experimental	Predicted
1	-1 (30)	-1 (30)	0 (15)	1.70	1.63
2	-1 (30)	1 (90)	0 (15)	1.10	0.97
3	1 (90)	-1 (30)	0 (15)	0.94	1.07
4	1 (90)	1 (90)	0 (15)	0.84	0.91
5	-1 (30)	0 (60)	-1 (5)	1.06	1.28
6	-1 (30)	0 (60)	1 (25)	0.84	0.82
7	1 (90)	0 (60)	-1 (5)	0.86	0.88
8	1 (90)	0 (60)	1 (25)	0.82	0.60
9	0 (60)	-1 (30)	-1 (5)	1.76	1.61
10	0 (60)	-1 (30)	1 (25)	1.06	1.15

Table 3. Final FFA (%) of CRBO Brand I after esterification based on BBD (cont.).

Run No.	X ₁ (Time, min)	X ₂ (MEOH:FFA)	X ₃ (% w/w FFA)	Brand I	
				Experimental	Predicted
11	0 (60)	1 (90)	-1 (5)	1.20	1.11
12	0 (60)	1 (90)	1 (25)	0.70	0.84
13	0 (60)	0 (60)	0 (15)	0.74	0.75
14	0 (60)	0 (60)	0 (15)	0.78	0.75
15	0 (60)	0 (60)	0 (15)	0.74	0.75

Table 4. Final FFA (%) of CRBO Brand II after esterification based on CCD.

Run No.	X ₁ (Time, min)	X ₂ (MEOH:FFA)	X ₃ (% w/w FFA)	Brand II	
				Experimental	Predicted
1	-1 (60)	-1 (20)	-1 (15)	1.68	1.85
2	1 (180)	-1 (20)	-1 (15)	3.06	3.14
3	-1 (60)	1 (50)	-1 (15)	1.02	1.18
4	1 (180)	1 (50)	-1 (15)	1.26	1.46
5	-1 (60)	-1 (20)	1 (25)	1.74	1.93
6	1 (180)	-1 (20)	1 (25)	2.82	3.04
7	-1 (60)	1 (50)	1 (25)	1.32	1.62
8	1 (180)	1 (50)	1 (25)	1.50	1.72
9	-1.68 (40.8)	0 (35)	0 (20)	1.24	0.93
10	1.68 (220.8)	0 (35)	0 (20)	2.34	2.09
11	0 (120)	-1.68 (9.8)	0 (20)	3.18	2.96
12	0 (120)	1.68 (60.2)	0 (20)	1.62	1.28
13	0 (120)	0 (35)	-1.68 (11.6)	2.28	2.10
14	0 (120)	0 (35)	1.68 (28.4)	2.76	2.39
15	0 (120)	0 (35)	0 (20)	1.38	1.42
16	0 (120)	0 (35)	0 (20)	1.44	1.42
17	0 (120)	0 (35)	0 (20)	1.38	1.42
18	0 (120)	0 (35)	0 (20)	1.38	1.42
19	0 (120)	0 (35)	0 (20)	1.44	1.42
20	0 (120)	0 (35)	0 (20)	1.38	1.42

Table 5. Final FFA (%) of CRBO Brand II after esterification based on BBD.

Run No.	X ₁ (Time, min)	X ₂ (MEOH:FFA)	X ₃ (% w/w FFA)	Brand II	
				Experimental	Predicted
1	-1 (30)	-1 (30)	0 (15)	1.44	1.42
2	-1 (30)	1 (70)	0 (15)	0.92	0.97
3	1 (90)	-1 (30)	0 (15)	1.00	0.94
4	1 (90)	1 (70)	0 (15)	0.84	0.85
5	-1 (30)	0 (50)	-1 (10)	1.64	1.54
6	-1 (30)	0 (50)	1 (20)	0.88	0.93
7	1 (90)	0 (50)	-1 (10)	0.92	0.86
8	1 (90)	0 (50)	1 (20)	0.92	1.01
9	0 (60)	-1 (30)	-1 (10)	1.12	1.23

Table 5. Final FFA (%) of CRBO Brand II after esterification based on BBD (cont.).

Run No.	X ₁ (Time, min)	X ₂ (MEOH:FFA)	X ₃ (% w/w FFA)	Brand II	
				Experimental	Predicted
10	0 (60)	-1 (30)	1 (20)	1.00	0.96
11	0 (60)	1 (70)	-1 (10)	0.88	0.92
12	0 (60)	1 (70)	1 (20)	0.84	0.73
13	0 (60)	0 (50)	0 (15)	0.92	0.85
14	0 (60)	0 (50)	0 (15)	0.84	0.85
15	0 (60)	0 (50)	0 (15)	0.80	0.85

3.2 Model evaluation

The coefficients of the developed models based on CCD and BBD using coded independent variables are presented in Table 6 and Table 7 along with related statistics. The CCD indicated that methanol-to-FFA molar ratio had the maximum effect on FFA conversion in both brands of CRBO as well as its interaction with reaction time in case of brand II. The CCD resulted in model fitting with low R²-value of about 0.669 for brand I with 8% FFA. However, the model fitting for brand II with 10% FFA was reasonably good with R²-value of about 0.904. A look at the final FFA values for both brands of CRBO revealed that the experimental conditions selected in CCD could not reduce the final FFA below the desired level of 1%.

Accordingly, the experimental conditions were adjusted in the direction of steepest gradient for use in the BBD as shown in Table 1. The results

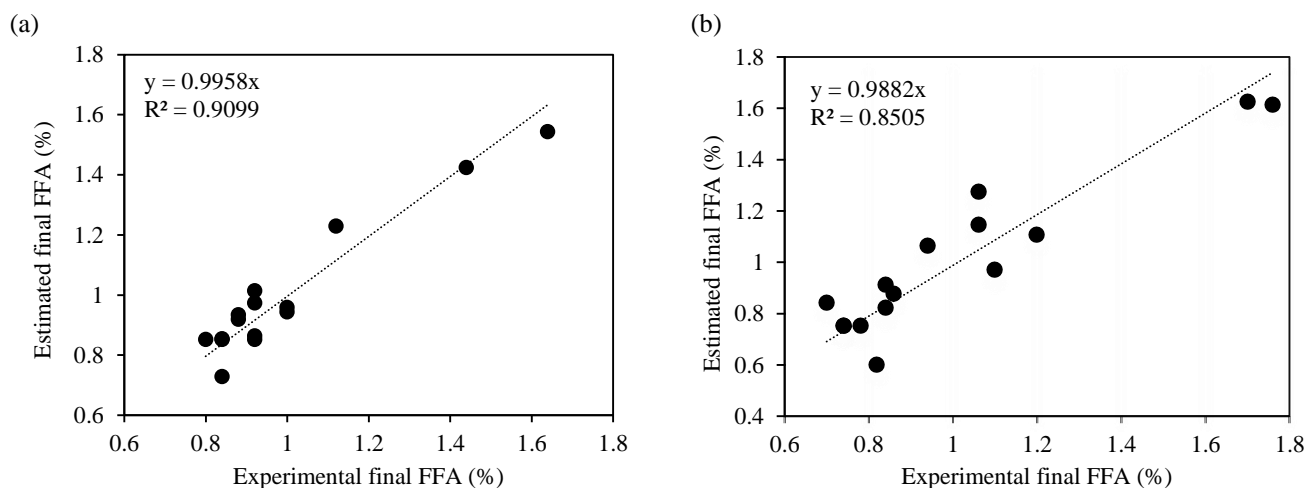
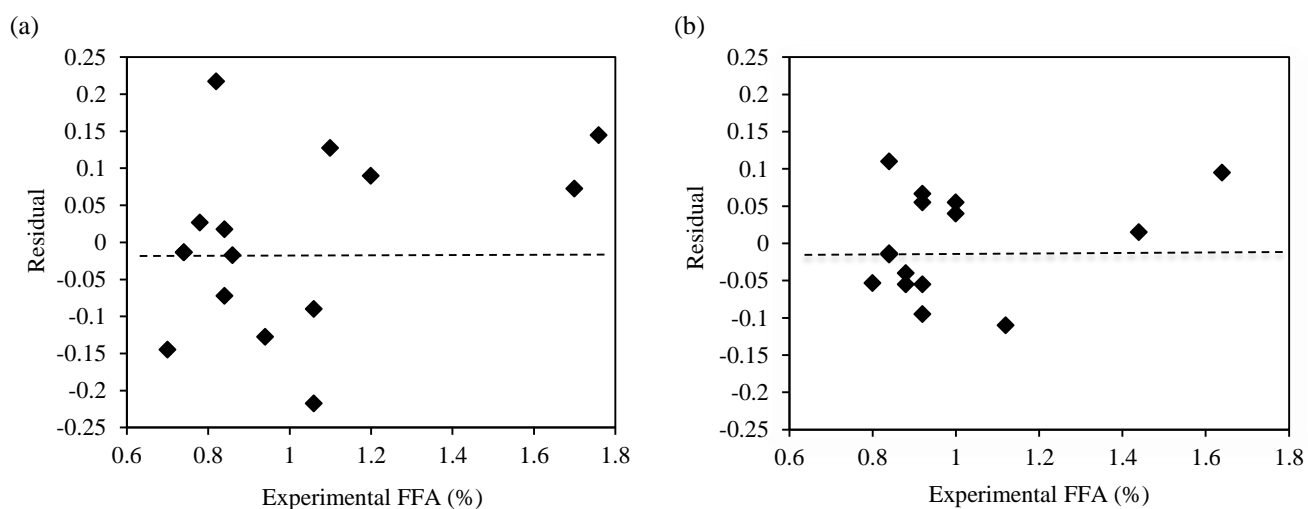
from 15 experiments runs of BBD in Table 3 clearly indicated the possibility of obtaining the final FFA levels less than 1%. Also there was a marked improvement in the fitting of models based on BBD for both brands of CRBO as shown by higher R²-value and lower SEE in Table 6 and Table 7. A comparison of experimental and estimated values of final FFA for both brands of CRBO based on BBD is presented in Figure 1. The results for CRBO brand I indicated higher variation compared to brand II despite the use of higher methanol-to-FFA molar ratio possibly due to its lower FFA content. Similar findings were reported by Chai et al. (2014) for esterification pretreatment of low FFA feedstocks requiring significantly higher methanol-to-FFA molar ratio. The residual plots for the prediction model developed using BBD clearly indicated random patterns in support of model acceptability for the both brands of CRBO as shown in Figure 2.

Table 6. Coefficients of models based on CCD and BBD for CRBO (Brand I).

Model coefficient	CCD	p-value	BBD	p-value
β_0	1.17	0.00	0.75	0.00
β_1	0.09	0.49	-0.15	0.08
β_2	-0.46	0.00	-0.20	0.03
β_3	-0.13	0.33	-0.18	0.05
β_{11}	0.17	0.21	0.05	0.63
β_{22}	0.22	0.11	0.34	0.02
β_{33}	0.13	0.30	0.09	0.43
β_{12}	-0.02	0.92	0.12	0.26
β_{13}	0.02	0.92	0.04	0.67
β_{23}	0.05	0.76	0.05	0.64
R ²	0.669		0.869	
R ² _{adj}	0.371		0.632	
SEE	0.467		0.199	
p-value (F>F crit)	0.112		0.083	

Table 7. Coefficients of models based on CCD and BBD for CRBO (Brand II).

Model coefficient	CCD	p-value	BBD	p-value
β_0	1.42	0.00	0.85	0.00
β_1	0.35	0.00	-0.15	0.01
β_2	-0.50	0.00	-0.13	0.02
β_3	0.09	0.30	-0.11	0.04
β_{11}	0.03	0.66	0.16	0.04
β_{22}	0.25	0.01	0.03	0.60
β_{33}	0.29	0.00	0.07	0.27
β_{12}	-0.25	0.03	0.09	0.18
β_{13}	-0.04	0.67	0.19	0.02
β_{23}	0.09	0.40	0.02	0.74
R^2	0.904		0.917	
R^2_{adj}	0.817		0.768	
SEE	0.287		0.114	
p-value (F>F crit)	0.001		0.030	

**Figure 1.** Comparison of experimental and estimated final FFA (%) for CRBO based on BBD, (a) Brand I; (b) Brand II.**Figure 2.** Residual plots for predicted final FFA (%) based on BBD, (a) Brand I; (b) Brand II.

3.3 Sensitivity analysis

The influence of esterification process parameters on the change in final FFA of two brands of CRBO is shown by the perturbation plots in

Figure 3 and Figure 4, respectively. These plots show the change in final FFA as each factor moves away from the center point (selected as reference) while holding other variables at the reference value.

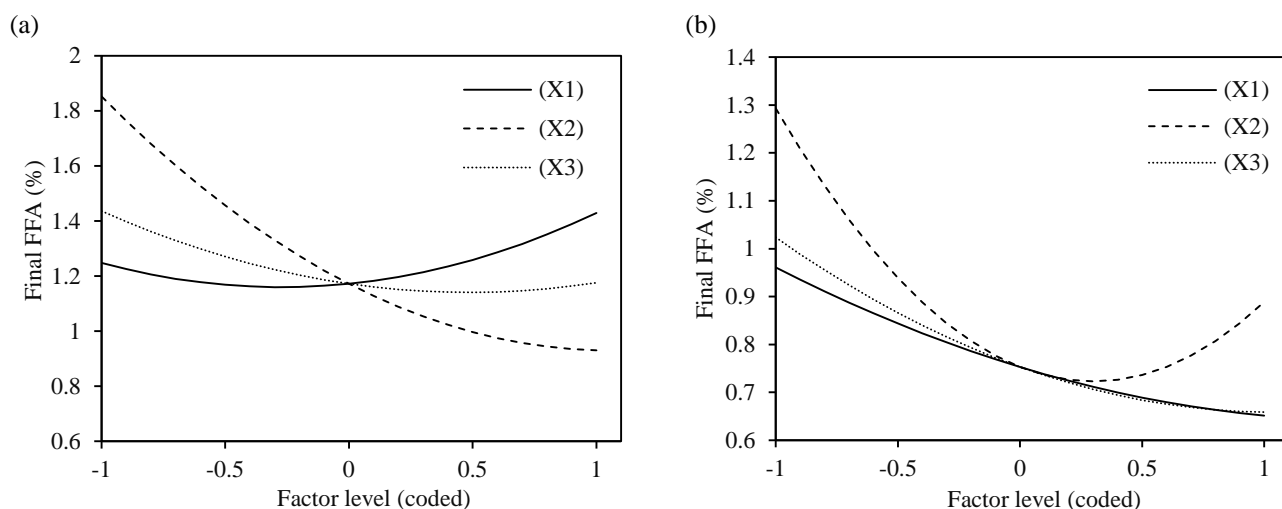


Figure 3. Perturbation plots for esterification of CRBO Brand, (a) CCD; (b) BBD.

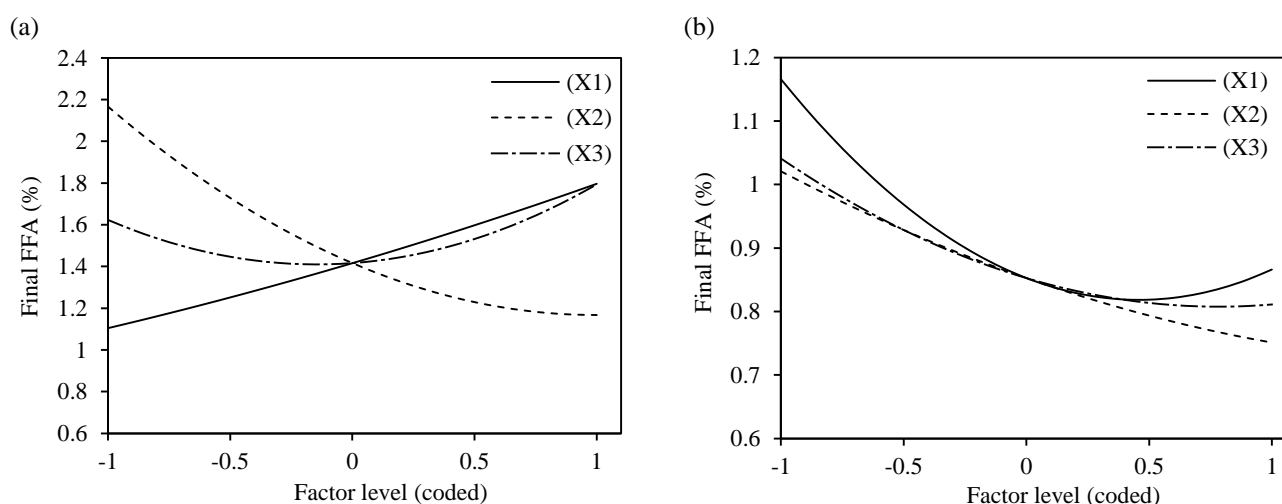


Figure 4. Perturbation plots for esterification of CRBO Brand II, (a) CCD; (b) BBD.

Figure 3 shows that final FFA (%) was most sensitive to the change in methanol-to-FFA molar ratio (X_2) for brand I of CRBO with 8% FFA compared to the reaction time (X_1) and amount of catalyst (X_3). Also the CCD based model required extreme conditions for reducing the final FFA less than 1%. Thus the model based on BBD showed distinct improvement in determining the optimal conditions for reduction in FFA. Figure 4 presents the results for Brand II of CRBO with 10% FFA. In this case also, the BBD showed clear improvement

over the CCD based model. However, the model based on CCD could depict the influence of linear and quadratic terms on the esterification process due to its sequential nature of experimentation.

3.4 Optimization

The models developed using BBD showed a significant improvement following the initial experimentation based on CCD. The optimum conditions for the esterification of CRBO are shown in Table 8 based on both CCD and BBD for

Table 8. Optimum conditions for esterification of CRBO.

CRBO brand	Model	Coded and actual values of independent variables			Initial FFA (%)	Final FFA (%)	FFA conversion (%)
		X ₁	X ₂	X ₃			
I	CCD	-0.2 ¹ (52.8)*	1.0 ² (90)*	0.3 ³ (18.1)*	8	0.91	88.6
	BBD	1.0 (90)	0.1 (61.7)	0.8 (22.6)	8	0.61	92.5
II	CCD	-1 (30)	0.5 (60.8)	-0.3 (13.5)	10	1.02	89.8
	BBD	-0.4 (48.1)	1.0 (70)	1.0 (20)	10	0.70	93.0

Note: (X₁)=time (min); (X₂)=methanol: FFA molar ratio; (X₃)=catalyst: FFA (% w/w); (¹)(²)(³)=coded values; (*)=actual values.

Table 9. Comparison of optimum process conditions for homogenous acid-catalyzed esterification of high FFA crude rice bran oil.

No.	Initial FFA (%)	Molar ratio (methanol:FFA)	Methanol (% w/w)	H ₂ SO ₄ (% w/w)	Time (min)	Temperature (°C)	Final FFA (%)	FFA conversion (%)	Reference
1	79 (Type I)	10:1	89.7	2	180	60	0.8	99	Amin et al. (2012)
6	(Type II)	10:1	6.8	2	180	60	3.2	46.7	
2	12	53.9:1	73.4	0.5	90	60	1.8	85	Arora et al. (2016)
3	8 (Step I)	7.05:1	6.4	0.5	60	55-60	1.8	90	Kattimani et al. (2014)
1.8	(Step II)	5.7:1	5.2	0.5	60	55-60	0.6	66.7	
4	20 (Step I)	9.7:1	22.0	1	60	60	2.4	88	Lin et al. (2009)
2.4	(Step II)	94.4:1	25.7	1	60	60	0.5	81.25	
5	49.8	3.2	18.4	2	120	60	3.2	93.57	Zullaikah et al. (2005)
6	8 (Brand I)	61.7:1	56.0	1.8	90	60	0.6	92.5	This study
10	(Brand II)	70:1	79.4	2	48.1	60	0.7	93	

comparative evaluation. The final FFA levels were predicted in 0.91-1.02% range by the CCD. However, the models based on BBD predicted significantly lower level of FFA in 0.61-0.70% range for both brands of CRBO. Thus, the reaction time, methanol-to-FFA molar ratio and amount of catalyst could be used in the respective ranges of 48-90 min, 60-70 methanol-to-FFA ratio and 20-23% H_2SO_4 : FFA (w/w) in general for lowering the high FFA in CRBO to an acceptable level in a single-step. It should be realized that more precise estimation of process variables is limited by the inherent errors in experimentation, especially when using titration method for FFA determination.

Several studies have reported the optimum conditions for the esterification of high FFA CRBO (Zullaikah et al., 2005; Lin et al., 2009; Amin et al., 2012; Kattimani et al., 2014; Arora et al., 2016). A direct comparison of optimization conditions reported in literature with the results of present study is not possible in an objective way due to very wide variation in the experimental conditions. However, the results reported in previous studies as well as the present study were expressed on the comparable basis as shown in Table 9.

In view of practical considerations, the amounts of (% w/w) of methanol and sulfuric acid as catalyst were computed based on 100 g of CRBO depending upon the initial FFA. The overall optimum conditions for the conversion of FFA in different CRBO samples in Table 9 showed the methanol use varying from 5.2 to 89.7% (w/w), sulfuric acid from 0.5 to 2%, and reaction time from 48.1 to 180 min for different initial FFAs and experimental conditions. While the two-step esterification can reduce the initial FFA to less than 1% as reported by Kattimani et al. (2014) and Lin et al. (2009), this study showed the reduction in FFA below 1% in a single-step process. The amount of methanol used in present study is comparable to that reported by Arora et al. (2016) even though the final FFA in their study was 1.8%. Also the amount of sulfuric acid used as catalysts ranged from 0.5 to 2% (w/w). These results also support the finding that higher methanol-to-FFA molar ratio is required for the conversion of low initial FFA in a variety of oil samples (Chai et al., 2014). Overall, the results of this study indicated a significant improvement in determining the optimum conditions for the esterification of CRBO with initial FFA in 8-10% range.

4. CONCLUSIONS

This study investigated the esterification of two brands of CRBO with high FFA content in 8-10% range. The DOE and RSM approach was effectively used for the acid-catalyzed esterification of CRBO with high FFA to obtain the final FFA less than 1% (w/w). The CCD could be used initially for investigating the relative effects of process conditions on FFA conversion through sequential experimentation leading to a distinct improvement in process conditions determined by BBD. The developed models accounted for the effects of reaction time, methanol-to-FFA molar ratio and catalyst concentration on the esterification process of CRBO with initial FFA in 8-10% range. The sensitivity analysis indicated that methanol-to-FFA molar ratio had the maximum effect on FFA conversion compared to the relatively minor effects of reaction time and catalyst amount. Higher methanol-to-FFA molar ratios were required to accomplish the conversion of high initial FFA to less than 1% in a single-step. The respective ranges of optimum conditions were 48-90 min of reaction time, 60-70:1 methanol-to-FFA molar ratio, and 20-25.5% catalyst based on FFA, and for final FFA reduction in approximately 0.6-0.7% range.

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