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Optimization of a two stage process for biodiesel production from shea butter using response surface methodology



E.O. Ajala ^{a,*}, F. Aberuagba ^b, A.M. Olaniyan ^c, M.A. Ajala ^d, M.O. Sunmonu ^e

^a Department of Chemical Engineering, University of Ilorin, Ilorin, Nigeria

^b Department of Chemical Engineering, Federal University of Technology, Minna, Nigeria

^c Department of Agricultural and Bioresources Engineering, Federal University, Oye-Ekiti, Nigeria

^d Department of Chemical Engineering, Ladoké Akintola University of Technology, Ogbomoso, Nigeria

^e Department of Food Engineering, University of Ilorin, Ilorin, Nigeria

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Abstract The challenges of biodiesel production from high free fatty acid (FFA) shea butter (SB) necessitated this study. The reduction of %FFA of SB by esterification and its subsequent utilization by transesterification for biodiesel production in a two stage process for optimization studies was investigated using response surface methodology based on a central composite design (CCD). Four operating conditions were investigated to reduce the %FFA of SB and increase the %yield of shea biodiesel (SBD). The operating conditions were temperature (40–60°C), agitation speed (200–1400 rpm), methanol (MeOH): oil mole ratio: 2:1–6:1 (w/w) for esterification and 4:1–8:1 (w/w) for transesterification and catalyst loading: 1–2% (H₂SO₄, (v/v) for esterification and KOH, (w/w) for transesterification. The significance of the parameters obtained in linear and non-linear form from the models were determined using analysis of variance (ANOVA). The optimal operating conditions that gave minimum FFA of 0.26% were 52.19°C, 200 rpm, 2:1 (w/w) and 1.5% (v/v), while those that gave maximum yield of 92.16% SBD were 40°C, 800 rpm, 7:1 (w/w) and 1% (w/w). The *p*-value of <0.0001 for each of the stages showed that the models were significant with R² of 0.96 each. These results indicate the reproducibility of the models and showed that the RSM is suitable to optimize the esterification and transesterification of SB for SBD production. Therefore, RSM is a useful tool that can be employed in industrial scale production of SBD from high FFA SB.

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1. Introduction

Global energy demand is increasing due to economic and technological development, as well as, population growth [1–4]. Meanwhile, the major source of energy currently is fossil fuel

* Corresponding author.

E-mail address: olawaleola01@yahoo.com (E.O. Ajala).

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with its attendant challenges such as global warming [3,5]. Biodiesel has been found as an alternative to fossil fuel. However, availability of sufficient feedstock for its production is a drawback. Biodiesel is produced from transesterification of refined vegetable oils such as Soybean, Rapeseed, Sunflower, and Palm oils, which are more costly than fossil diesel [4,6]. More so that the biodiesel production from these refined and edible vegetable oils can lead to food oil crisis [1]. Therefore, biodiesel derived from refined and edible oil are not sustainable, but using cheap and non-edible feedstock such as *Jatropha*, animal fats, and waste cooking oil as well as unrefined crude edible oil like shea butter have been suggested as an alternative feedstock [7,8]. Biodiesel made from these feedstocks were predicted to be economically viable than that of the refined oil [9].

The SB generally consists of more than 90% triglycerides, of which 41.1% is saturated fatty acids which are a good property for biodiesel production [10]. The saturated fatty acids make a high cloud point, high cetane number, good stability, and quality biodiesel. Another advantage of SB for biodiesel production is that it undergoes less oxidation reaction since it contains tocopherols and phenolic compounds which are natural anti-oxidant [11]. Hence, SB for biodiesel production can make a good alternative fuel in compression ignition engines. However, high consumption of catalyst and formation of soap with a low yield of biodiesel due to high FFA (> 1%) and moisture content (> 0.5%) in SB are the challenges for its use for biodiesel production [9,12,13]. This is due to unwanted saponification reaction that takes place as side reaction and makes the purification of biodiesel difficult, thereby increases the overall cost of biodiesel production [6,8,13,14]. Nevertheless, SB is a suitable alternative to the refined oil due to its abundant availability and aforementioned composition which make a quality biodiesel.

Successful SBD production can be achieved by reducing the percentage content of FFA in SB to < 1%. This can be done in an esterification process with the aid of an acid catalyst by a reversible reaction between carboxylic acid and alcohol to give at least one ester product and water [15]. Thereafter, the transesterification process of the SB with FFA < 1% (also known as esterified shea butter, ESB) follows, in the presence of a base catalyst using excess alcohol to shift the equilibrium to favor production of SBD. Therefore, to attain greater yield and quality SBD from high FFA SB, an appropriate quantity of alcohol (methanol) in mole ratio with oil is required. Adequate catalyst loading, proper agitation speed and moderate temperature are also required to obtain a higher yield of SBD through esterification and transesterification reactions. However, excess methanol, higher temperature, and too much agitation speed can lead to wastage of resources. Despite the aforementioned, insufficient catalyst can cause incomplete conversion of SB and lower the yield of SBD while excess catalyst can lead to soap formation, thereby hampering the yield of SBD [4], hence the need for optimization study using response surface methodology (RSM).

The RSM is an effective and important tool for statistical analysis to find the optimal conditions for different complex processes, which has been applied in the optimization of multiple variables with a minimum number of experiments [16,17]. Meanwhile, the central composite design (CCD) of RSM has been applied in the optimization of several chemical and technological processes. The benefit of the CCD of RSM is in the reduction of experimental runs that would provide sufficient

data to generate enough information for a statistically acceptable result. RSM has been successfully used for the optimization of esterification and transesterification of beauty leaf (*Calophyllum inophyllum*) and *Jatropha caucis* for biodiesel production [4,18].

The present study, therefore, investigates the effect of temperature, MeOH: oil mole ratio, catalyst loading and agitation speed on optimization studies using RSM for esterification and transesterification reactions in a two stage process to reduce the %FFA of SB and improve the %yield of SBD respectively.

2. Materials and methods

2.1. Materials

Shea butter with FFA of 6.86% was purchased from Ilorin South of Kwara State, Nigeria. The chemicals used were of analytical grades. A 4.5 L reactor developed at the Engineering Workshop of the University of Ilorin was used for the study. The reactor was made of stainless steel and had heater band with a temperature and electric motor speed controllers.

2.2. Experimental design for the esterification and transesterification of SB

A three-level-four-factor CCD of RSM with design expert (version 8.06 Stat-Ease Inc., Minneapolis, MN) was used for both esterification and transesterification process. A total number of 30 experiments were designed for each of the stages to determine the %FFA and %yield of SBD using ranges of variables as reaction temperature (A) (40–60°C), agitation speed (B) (200–800 rpm), MeOH: oil mole ratio (C) (2:1–6.1 (w/w)) for esterification and 4:1–8:1 (w/w) for transesterification, and catalyst loading (D) (0.5–1.5 (%)) of H₂SO₄ (v/v) for esterification and KOH (w/w) for transesterification. The ranges for each of the variables were chosen based on the preliminary studies.

2.3. Esterification process

The SB was filtered after melting, to remove impurities and heated to 100°C for 10 min to eliminate moisture and obtained pure SB. Two thousand grams of the pure SB was measured and reacted with MeOH in the varying range aforementioned using H₂SO₄ as a catalyst at 50°C and varying agitation speed in the reactor. After 4 h, the unreacted MeOH was removed from the reaction mixture by a vacuum distillation at 65°C and the mixture of the product was allowed to separate into an upper organic phase and a lower aqueous catalyst phase [13]. The refined oil was analyzed for %FFA (< 1%) and collected for the transesterification.

2.4. Transesterification process

The ESB (%FFA < 1) was transesterified using MeOH (solvent) and KOH (catalyst) to synthesize SBD at a reaction time of 2 h [19]. The product was discharged into a separating funnel, cooled and settled for 24 h. The SBD was separated from glycerol to obtain crude biodiesel and was thereafter purified.

Table 1 Physico-chemical Properties of SBD as Compared with Diesel and the ASTM Specifications.

Property	SBD	Diesel	ASTM method	Limits
Density kg/m ³ @15 °C	883.0	860.4	4052-11	860–900
Specific gravity kg/m ³ @15 °C	883.4	860.8	4052-11	
Kinematic viscosity mm ² /s@40 °C	5.93	2.6	445-12	1.9–6.0
Flash point (°C)	130.0	73.0	93-02a	130 min
Cloud point (°C)	12	2.4	2500-11	–3 to 12
Pour point (°C)	10	–9	97-12	–15 to 10
Cetane	47	49	976-11	47–60
Total sulfur (% mass)	0.001	0.300	4294-10	0.005 max
Water content (% vol.)	< 0.05	< 0.05	95-13	0.05 max
Color	L0.5	L2.0	1500-12	L2.0
Total acid value (mg KOH/g)	0.16		974-12	0.80 max
Distillation IBP	220.0	176.0	86-12	
Distillation 90% recovery °C	342.0	341.0	–	360 max
Distillation FBP	352.0	365.0	–	
Recovery (%)	98.5	98.5	–	90 min
Residue	1.0	1.0	–	
Loss	0.5	0.5	–	
Diesel index	30	28	IP21	
Aniline point (°F)	104.0	86	611-12	

Source: Ajala et al. [19].

2.5. Statistical analysis

The experimental data obtained from the experimental procedure of the two stages were analyzed by the response surface regression approach of second-order polynomial equation (Eq. (1)).

The results obtained from the experimental design of the study using the design expert was used to generate polynomial equations which were analyzed to predict the %FFA and % yield of SBD as the dependent variables, and temperature, agitation speed, MeOH: oil mole ratio and catalyst loading as the independent variables for the two stages. The data generated were thereafter subjected to analysis of variance (ANOVA). The significance of the models and the independent variables were accordingly determined.

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} x_i x_j \quad (1)$$

Where Y represents the predicted response; β_0 is the offset term; β_i is the linear coefficient; β_{ii} is the second-order coefficient and β_{ij} is the interaction coefficient; x_i and x_j are the independent variables.

2.6. Analysis of the samples

The FFA content of the SB was determined using the standard method reported by Chopra and Kanwar [20]. The %yield of SBD was obtained using Eq. (2):

$$\text{Yield of SBD}(\%) = \frac{\text{Total weight of methyl esters formed}}{\text{Total weight of oil used}} \times 100\% \quad (2)$$

The SBD produced from this study has been characterized for physicochemical properties. The following properties were determined: density, specific gravity, kinematic viscosity, flash point, cloud and pour points, cetane number, total sulfur,

water content, total acid value and color using ASTM standards. The results have been published by the author as reported in Table 1 [19]. The Fatty Acid Methyl Esters (FAME) compositions were determined using GC-MSD equipped with triple axis detector and auto-sampler injector. Two hundred and fifty milligrams of the SBD sample was weighed into a sample bottle and the sample was injected at split mode (50:1) through a highly polar Agilent 190925-433 capillary column and 30 m length to perform the analysis. The spectra were obtained and compared with those of the standard spectra from NIST library (NIST 11) [19]. The results of FAMES have been published by the author as shown in Table 2 [19].

3. Results and discussion

3.1. Optimization of esterification reaction of high FFA SB

The %FFA obtained from the esterification is the response (Y) with the minimum obtainable as 0.26% from Exp. Run 14 as shown in Table 3.

Linear model: The temperature (A), agitation speed (B), MeOH: SB mole ratio (C) and catalyst loading (D), each of

Table 2 GC–MS Quantitative Analysis of FAME Composition of SBD.

S/N	Retention time (min)	FAMES	Molecular formula	% Composition
1	24.5	Methyl palmitate	C16:0	25.6
2	27.6	Methyl linoleate	C18:2	7.53*
3	28.0	Methyl oleate	C18:1	–
4	28.5	Methyl stearate	C18:0	46.32
5	31.3	Methyl gondoate	C20:1	4.55*
6	31.7	Methyl arachidate	C20:0	14.04
7	34.9	Methyl behenate	C24:0	1.95

Source: Ajala et al. [19].

* Monosaturated Fatty Acid Methyl Esters.

Table 3 Predicted and Actual Results of CCD for Esterification Process.

Exp.	Temp. (°C)	Agitation (rpm)	MeOH: SB mole ratio (w/w)	Catalyst (H ₂ SO ₄ , v/v)	%Free Fatty Acid	
					Actual Response	Predicted Response
1	40	200	2	0.50	4.50	4.48
2	60	200	2	0.50	2.60	2.82
3	40	1400	2	0.50	3.07	3.03
4	60	1400	2	0.50	2.40	2.11
5	40	200	6	0.50	1.48	1.42
6	60	200	6	0.50	0.98	0.72
7	40	1400	6	0.50	0.35	0.41
8	60	1400	6	0.50	0.28	0.44
9	40	200	2	1.50	3.80	3.58
10	60	200	2	1.50	1.30	1.17
11	40	1400	2	1.50	2.49	2.67
12	60	1400	2	1.50	0.98	0.98
13	40	200	6	1.50	1.50	1.71
14	60	200	6	1.50	0.28	0.26
15	40	1400	6	1.50	1.50	1.23
16	60	1400	6	1.50	0.56	0.51
17	40	800	4	1.00	4.80	4.96
18	60	800	4	1.00	3.40	3.77
19	50	200	4	1.00	1.10	1.37
20	50	1400	4	1.00	0.52	0.78
21	50	800	2	1.00	2.40	2.70
22	50	800	6	1.00	0.70	0.93
23	50	800	4	0.50	1.00	1.23
24	50	800	4	1.50	0.52	0.82
25	50	800	4	1.00	2.60	2.19
26	50	800	4	1.00	2.30	2.19
27	50	800	4	1.00	2.60	2.19
28	50	800	4	1.00	2.20	2.19
29	50	800	4	1.00	2.40	2.19
30	50	800	4	1.00	2.60	2.19

Table 4 Estimated Coefficients of the Fitted Quadratic Model for the %FFA Reduction of SB.

Factors	%FFA of SB		
	Coefficients	F-value	p-value
Intercept	2.19	28.40	< 0.0001
A	-0.60	59.23	< 0.0001
B	-0.30	15.00	0.0015
C	-0.88	130.70	< 0.0001
D	-0.21	7.18	0.0171
AB	0.18	4.99	0.0412
AC	0.24	8.61	0.0103
AD	-0.19	5.33	0.0356
BC	0.11	1.70	0.2121
BD	0.13	2.59	0.1286
CD	0.30	13.11	0.0025
A ²	2.18	114.33	< 0.0001
B ²	-1.11	29.73	< 0.0001
C ²	-0.37	3.32	0.0886
D ²	-1.16	32.46	< 0.0001

the variables gave p value of < 0.05 as shown in Table 5; an indication that in their linear form, they are highly significant.

Non-linear model: The interactions effect between temperature and agitation speed, temperature and catalyst loading, and MeOH: SB mole ratio and catalyst loading were also significant with $p < 0.05$. The quadratic effect of temperature,

Table 5 Coefficient of Regression Analysis for Esterification Process.

Regression	Value
R-Square	0.9637
Adjusted R-Square	0.9297
Predicted R-Square	0.8467
Coefficient of Variance	17.20%

agitation speed, and catalyst loading was significant with $p < 0.0001$ (Table 4).

The effect of these variables on the %FFA reduction with $p < 0.0001$ for the model implies its significance. The value of regression coefficient (R^2) for the model as shown in Table 5 was 0.9637, which indicates the good fitness of the model. The predicted R^2 was 0.8467 which also corroborates the reliability of the model.

3.2. Effect of temperature, agitation speed, catalyst loading and methanol: oil mole ratio on %FFA reduction

Figs. 1–3 show the effect of temperature as it interacts with other variables on %FFA reduction. The figures showed that the minimum %FFA was achieved at a temperature of 50°C, agitation speed of 200 and 1400 rpm. This is because moderate

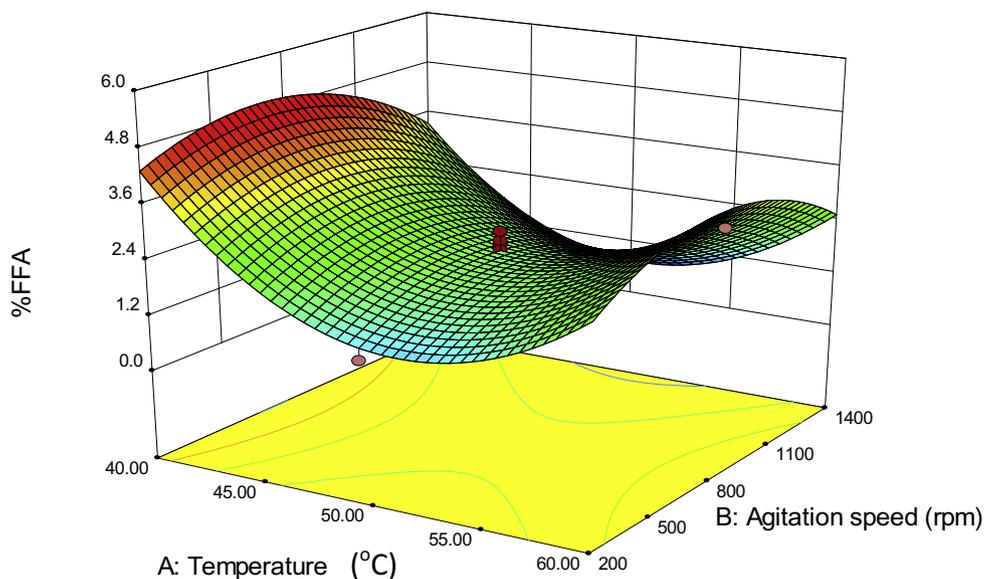


Figure 1 Effect of Temperature ($^{\circ}\text{C}$) and Agitation speed (rpm) on %FFA reduction at MeOH: SB mole ratio (w/w) of 4:1 and Catalyst loading of 1% (v/v).

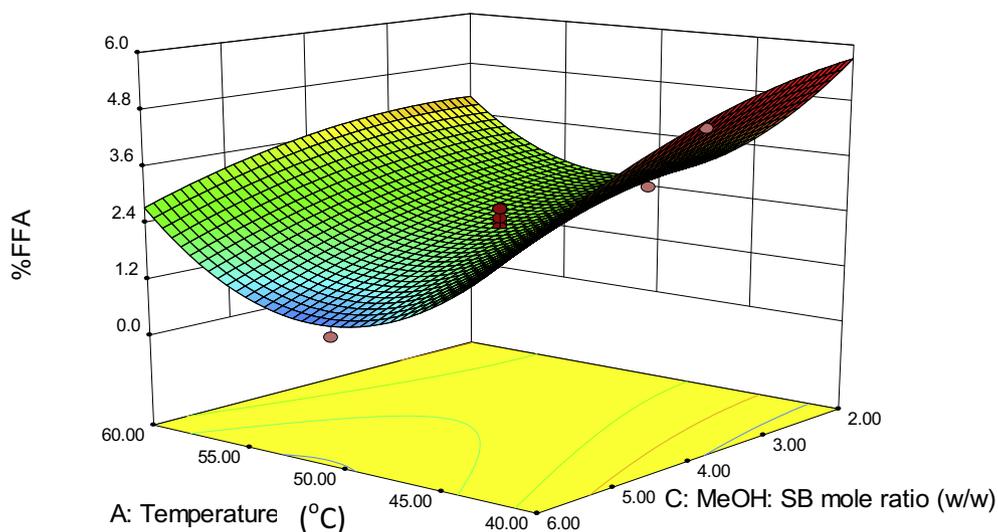


Figure 2 Effect of Temperature ($^{\circ}\text{C}$) and MeOH: SB mole ratio (w/w) on %FFA Reduction at Agitation speed of 800 rpm and Catalyst loading of 1% (v/v).

temperature increases the solubility of oil in methanol and reduces the %FFA in the shea butter. This indicates that temperature below and above 50°C have an inhibitive effect on the reduction of FFA content. Figs. 4 and 5 show the effect of agitation speed as it interacts with MeOH: SB mole ratio and catalyst loading respectively. The figures showed that the reduced %FFA of 0.52% was obtained at a catalyst loading of 1.5% (v/v) and increases as the catalyst loading decreases. So, the temperature of 50°C and catalyst loading of 1.5% (v/v) favored the reduction of %FFA in SB. Fig. 4 is the plot of %FFA against agitation speed and MeOH: SB mole ratio. It was observed that an increase in agitation speed with an increase in MeOH: SB mole ratio gave minimum %FFA. At a lower agitation speed and MeOH: SB mole ratio, the %

FFA increases. This indicates that the interaction of agitation speed and MeOH: SB mole ratio has an effect on the reduction of %FFA of SB. There was also a significant effect on %FFA reduction when agitation speed and catalyst loading interact (Fig. 5). The figure shows that the %FFA reduction of 0.52 was obtained at an agitation speed of 800 rpm and catalyst loading of 1.50% (v/v). Fig. 6 shows the effect of catalyst loading and MeOH: SB mole ratio on the %FFA reduction. When catalyst loading was 0.50% (v/v) and MeOH: SB mole ratio was 6:1 (w/w), %FFA decreased. As the catalyst loading increased to 1% (v/v) and MeOH: SB mole ratio was 6:1 (w/w), the %FFA also increased. This is due to the decomposition of SB at high catalyst loading and moderate MeOH: SB mole ratio, as a further increase in catalyst loading to 1.5%

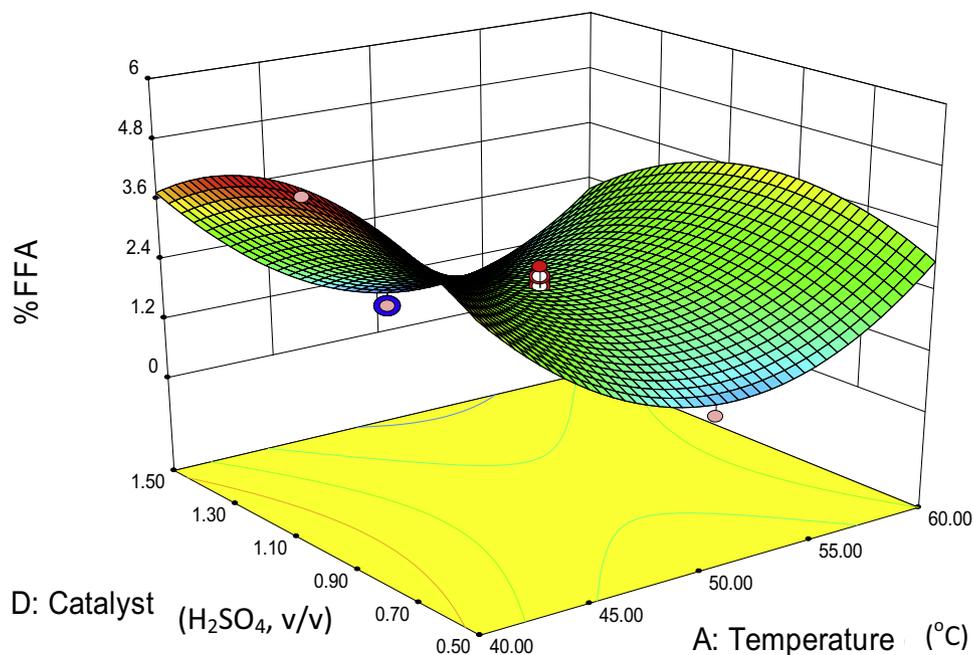


Figure 3 Effect of Temperature ($^{\circ}\text{C}$) and Catalyst loading on %FFA Reduction at Agitation speed of 800 rpm and MeOH: SB mole ratio of 4:1 (w/w).

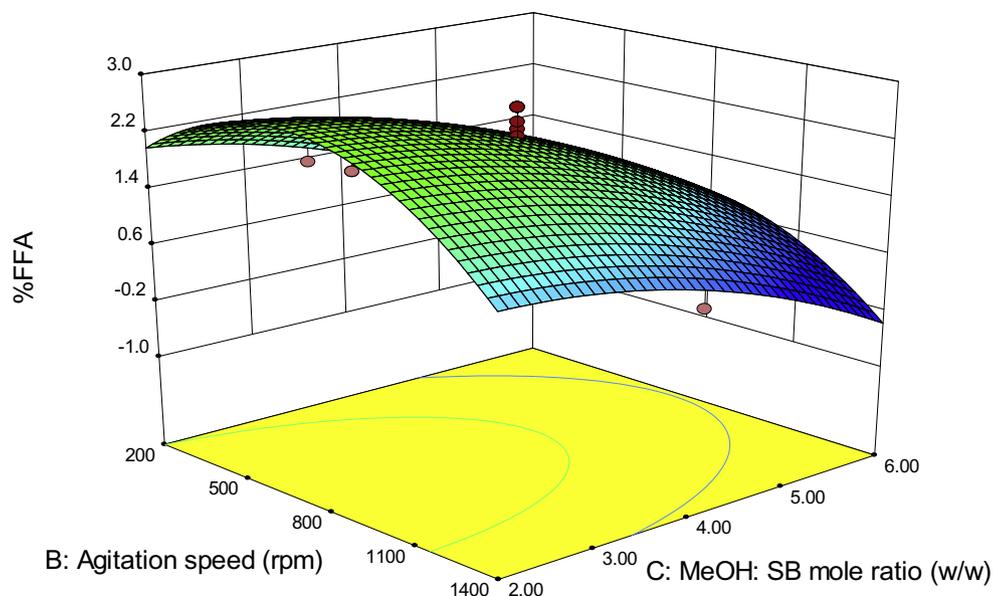


Figure 4 Effect of Agitation speed (rpm) and MeOH: SB mole ratio (w/w) on %FFA Reduction at Temperature of 50°C and Catalyst loading of 1% (v/v).

(v/v) and MeOH: SB mole ratio of 4:1 (w/w) gave minimum FFA of 0.52%. Table 6 shows the predicted optimal variables with the FFA of 0.27%. The predicted optimal parameters were validated by repeating the experiment in triplicate and obtained an average value of 0.26% FFA. The %error is 3.85, which is within the allowable limit. This showed that the model is reproducible and sufficiently described the esterification process.

The regression Eq. (3) for the determination of predicted values of output parameter (FFA) is given as:

$$\begin{aligned}
 FFA(\%) = & -145.92419 + 2.96975 \times A + 24.39775 \times B \\
 & + 0.28219 \times C - 0.048500 \times A \times B + 1.73333E \\
 & - 003 \times A \times C + 3.85417E - 003 \times B \times C \\
 & - 0.028027 \times A^2 - 1.64631 \times B^2 - 1.13479E \\
 & - 003 \times C^2
 \end{aligned} \quad (3)$$

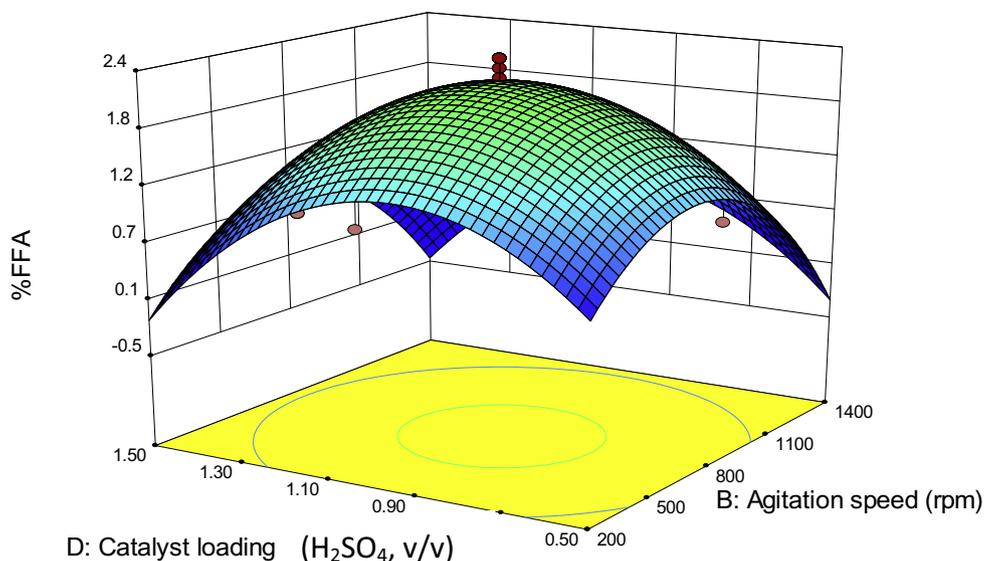


Figure 5 Effect of Agitation speed (rpm) and Catalyst loading (v/v) on %FFA Reduction at Temperature of 50°C and MeOH: SB mole ratio of 4:1 (w/w).

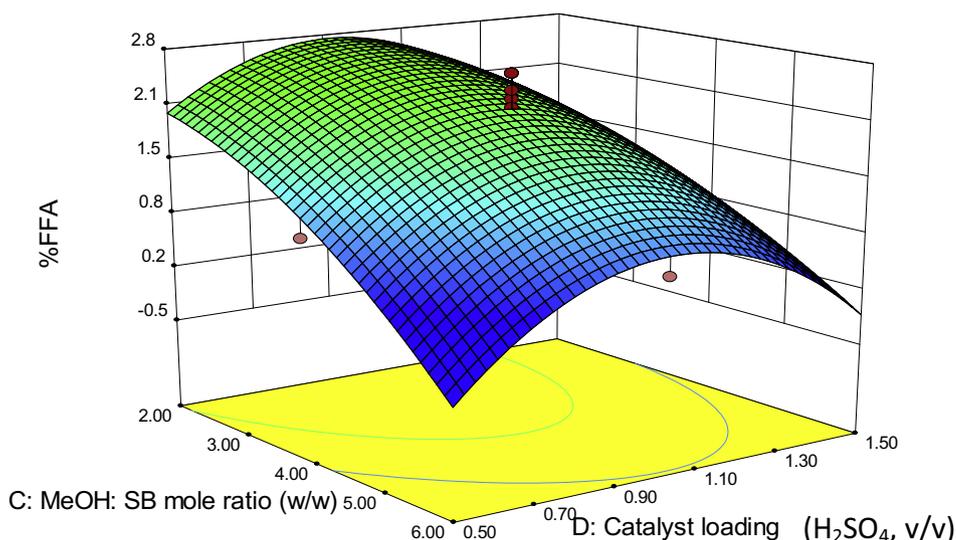


Figure 6 Effect of MeOH: SB mole ratio (w/w) and Catalyst loading (v/v) on %FFA Reduction at Temperature of 50°C and Agitation speed of 800 rpm.

where A–D are the variables in term of temperature (°C), agitation speed (rpm), methanol: SB mole ratio (w/w) and catalyst loading (w/w) respectively.

3.3. Optimization of transesterification reaction of ESB

The %yield of SBD from ESB with the experimental design matrix of the variables is shown in Table 7. The experimental run 7 gave the highest %yield of 90.87% SBD. A quadratic polynomial equation obtained from the experimental design analysis is presented as Eq. (4), which is in terms of the coded factors that predicted the %yield of SBD.

$$\begin{aligned} \%BiodieselYield\left(\frac{w}{w}\right) = & +79.82 - 4.09 \times A - 1.81 \times B + 2.52 \times C \\ & - 6.49 \times D - 2.30 \times A \times B - 2.24 \times A \times C \\ & - 2.45 \times A \times D + 6.25E - 004 \times B \times C \\ & - 1.70 \times B \times D - 1.25 \times C \times D - 1.47 \\ & \times A^2 - 6.99 \times B^2 + 0.017 \times C^2 + 3.16 \times D^2 \end{aligned} \tag{4}$$

where A–D are the variables in term of temperature (°C), agitation speed (rpm), methanol: ESB mole ratio (w/w) and catalyst loading (w/w) respectively.

Table 6 Optimal Parameters for Esterification of High FFA SB.

Parameters	Optimum Level	Low Level	High Level
A Temperature (°C)	52.19	40.00	60.00
B Agitation Speed (rpm)	200.72	200.00	1400.00
C Mole Ratio (w/w)	2.03	2.00	6.00
D Catalyst (H ₂ SO ₄ , v/v)	1.46	0.50	1.50
<i>Percentage Free Fatty Acid (%FFA)</i>			
Predicted Result	0.27	0.28	4.80
Empirical Result	0.26		
Percentage error	3.85		

The results of ANOVA for fitting the second-order response surface model by a mean square method are shown in Table 8. The coefficients of the response surface model as provided in Eq. (4) were evaluated. The *p*-values of all the coefficients and their significance are shown in Table 9. The *p*-values of the model and all the coefficients in the study, except BC, A² and C² showed that they are statistically significant. These results reflect the importance of the variable considered in this study. The F-value was 37.50 which is relatively high with a very low *p*-value of <0.0001. The “Lack of Fit value” of 0.96 was obtained, which implies the Lack of Fit is not significant relative to the pure error. The low C.V of 2.34% fur-

ther established that the fitted model is reliable. The R² obtained was 0.9722 which is an indication that 97% of the experimental data are compatible with the predicted data of the model. The Adj. R² was 0.9967, which is also very high, supporting the significance of the model.

3.4. Effect of variable parameters on % Yield of SBD

3.4.1. Effect of interaction of temperature with other variables on %yield of SBD

The combined effect of temperature and agitation speed on SBD production from ESB at MeOH: ESB mole ratio 6:1 (w/w) and catalyst loading (KOH) 1.5% (w/w) is shown in Fig. 7. At a low temperature of 40°C and agitation speed of 200 rpm, the yield of SBD was 74%, but when the agitation speed was increased to 800 rpm at 40°C, the %yield of SBD increased to 82.5%. A further increase in agitation speed to 1400 rpm reduced the yield of SBD to 75%. The lower %yield of SBD at 200 and 1400 rpm as compared with 800 rpm is due to the homogenization between the ESB and methanol which is less smooth at low agitation speed (200 rpm) and increase in turbulence within the medium at high agitation speed (1400 rpm) that has the high potential to produce soap reaction, whereas, at a moderate agitation speed of 800 rpm, transesterification reaction increases the frequency of collisions between reactant molecules and accelerates the reaction process with a greater yield of SBD [21]. The combined effect of

Table 7 Predicted and Actual Results of CCD for Transesterification Process.

Exp.	Temp. (°C)	Agitation (rpm)	MeOH: ESB mole ratio (w/w)	Catalyst (KOH, w/w)	%Yield of SBD	
					Actual Response	Predicted Response
1	40	200	4	1.00	73.58	74.46
2	60	200	4	1.00	81.42	80.28
3	40	1400	4	1.00	80.12	78.85
4	60	1400	4	1.00	74.15	75.47
5	40	200	8	1.00	85.32	86.48
6	60	200	8	1.00	84.04	83.34
7	40	1400	8	1.00	91.86	90.87
8	60	1400	8	1.00	77.79	78.53
9	40	200	4	2.00	73.22	72.29
10	60	200	4	2.00	67.50	68.29
11	40	1400	4	2.00	69.36	69.86
12	60	1400	4	2.00	58.02	56.67
13	40	200	8	2.00	80.83	79.31
14	60	200	8	2.00	65.28	66.36
15	40	1400	8	2.00	75.94	76.89
16	60	1400	8	2.00	55.82	54.74
17	40	800	6	1.50	81.23	82.44
18	60	800	6	1.50	73.91	74.27
19	50	200	6	1.50	74.25	74.64
20	50	1400	6	1.50	69.86	71.03
21	50	800	4	1.50	76.11	77.32
22	50	800	8	1.50	82.01	82.36
23	50	800	6	1.50	84.49	79.82
24	50	800	6	2.00	74.93	76.49
25	50	800	6	1.50	79.96	79.82
26	50	800	6	1.50	80.25	79.82
27	50	800	6	1.50	79.81	79.82
28	50	800	6	1.50	80.34	79.82
29	50	800	6	1.50	79.21	79.82
30	50	800	6	1.50	79.40	79.82

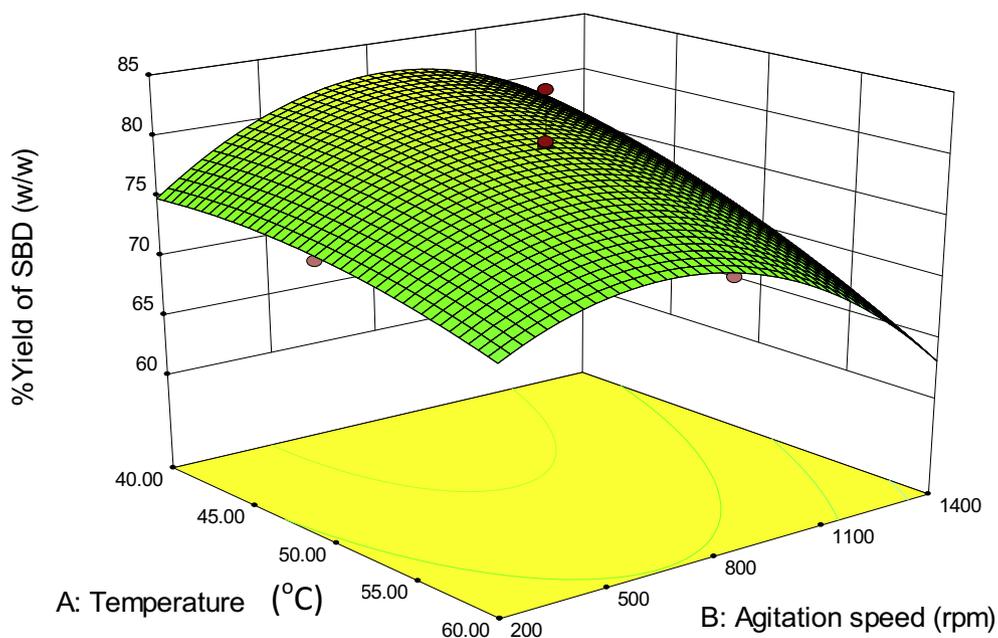
Table 8 ANOVA for %Yield of SBD.

Source	Sum of square	Df	Mean square	F	<i>p</i> – value
Regression	1674.33	14	119.59	37.50	< 0.0001
Linear	1107.66	4	276.92	11.27	< 0.0001
Square	234.21	4	58.55	18.36	< 0.0001
Interaction	332.45	6	55.41	3.73	0.0127
Residue error	47.84	15	3.19		
Lack of fit	28.19	9	3.13	0.96	0.5431 Not sig.
Pure error	19.65	6	3.27		
Total	1722.17	29			
R ² 0.9722	Adj. R ² 0.9463	Pred. R ² 0.8591		C.V. 2.34%	

Table 9 Estimated Coefficient of the Model and Variables for %Yield of SBD.

Factors	%Yield of SBD		
	Coefficient	F-value	<i>p</i> -value
Intercept	79.82	37.50	< 0.0001
A	-4.09	94.18	< 0.0001
B	-1.81	18.42	0.0006
C	2.52	35.92	< 0.0001
D	-6.49	214.87	< 0.0001
AB	-2.30	26.52	0.0001
AC	-2.24	25.16	0.0002
AD	-2.45	30.19	< 0.0001
BC	0.00063	1.96×10^{-6}	0.9989
BD	-1.70	14.55	0.0017
CD	-1.25	7.81	0.0136
A ²	-1.47	1.61	0.2239
B ²	-6.99	36.24	< 0.0001
C ²	0.017	2.264×10^{-4}	0.9882
D ²	3.16	4.92	0.0424

temperature and MeOH: mole ratio on the %yield of SBD at an agitation speed of 800 rpm and catalyst loading (KOH) of 1.5% (w/w) is shown in Fig. 8. It can be observed from the figure that the %yield of SBD increases from 70 to 87% with an increase in MeOH: ESB mole ratio from 4:1 to 8:1. The increase in the SBD yield is due to better dispersion of the ionic liquid of the catalyst and oil, which promotes the catalyst activity [22]. Also, since the reaction of ESB and MeOH is a reversible reaction, excess MeOH in the ratio of 8:1 to ESB is required to shift the equilibrium toward the direction of SBD production [23,24]. The result obtained in this study was in agreement with the report of Srilatha et al. [25]. The increase in the temperature from 40 to 60°C also showed a decline in the %yield of SBD. This is because as the reaction temperature closes to MeOH boiling point (64.7°C), the net amount of MeOH available for transesterification decreases, due to quick evaporation. Also, a higher reaction temperature accelerates the saponification reaction of triglycerides to form soap, hence reduces the %yield of SBD [24]. Therefore, at MeOH: ESB mole ratio of 8:1 and temperature of 40°C, the optimum yield of 87% SBD was obtained. This showed that the %yield of SBD increases with an increase in MeOH:

**Figure 7** Effect of Temperature and Agitation speed on %Yield of SBD using ESB.

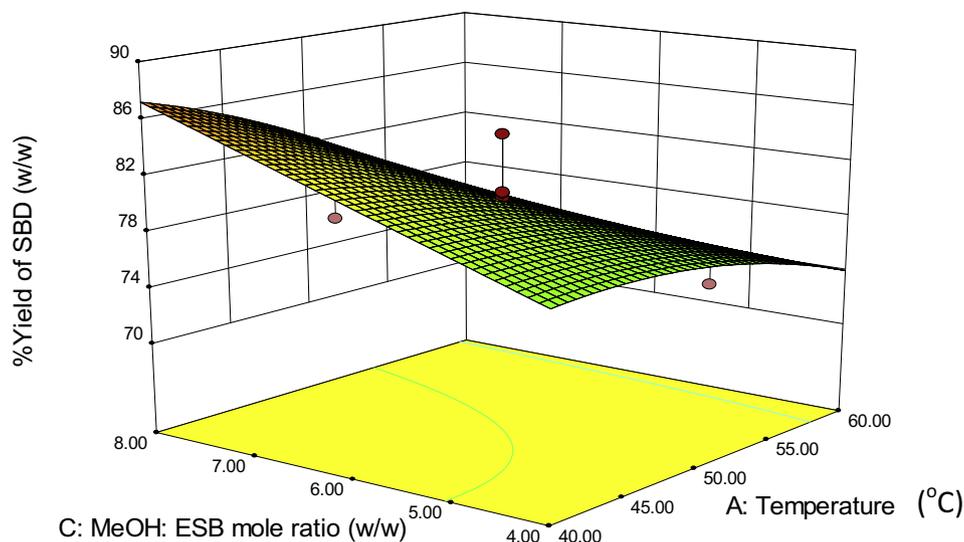


Figure 8 Effect of Temperature and MeOH: ESB ratio on %Yield of SBD.

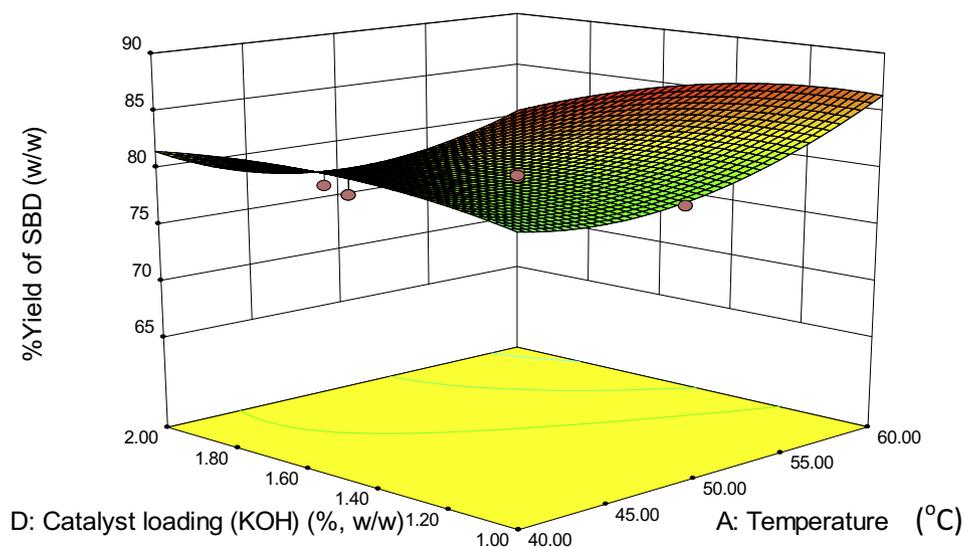


Figure 9 Effect of Temperature and Catalyst loading on %Yield of SBD using ESB.

ESB mole ratio, at reduced temperature. This result conforms to the results reported by Goyal et al. [18]. Fig. 9 shows the combined effect of temperature and catalyst loading at an agitation speed of 800 rpm and MeOH: ESB mole ratio of 6:1 w/w on %yield of SBD. At a low temperature of 40°C, the increase in the yield of SBD was almost negligible with an increase in catalyst loading from 1 to 2% (w/w). The maximum 86% yield of SBD was obtained at a catalyst loading of 1% (w/w) and temperature of 60°C. These results showed that temperature significantly affects the yield of SBD, due to the fact that MeOH is at the subcritical state and its solubility is not close to that of oil because at 60°C there is a single phase between oil and methanol which might have allowed the catalyst to be active. This result corroborates with the finding of Momoh et al. [26]. A further increase in catalyst loading to 2% (w/w) at 60°C gave the lowest yield of 70% SBD. This

was due to the reverse reaction as a result of the excess amount of catalyst which led to soap formation, as soap formation occurs at a higher catalyst loading above 1.5% (w/w) [22,27].

3.4.2. Effect of interaction of MeOH: ESB mole ratio with other variables on %yield of SBD

The combined effect of MeOH: ESB mole ratio and agitation speed is shown in Fig. 10. The figure showed that the %yield of SBD increases to 82.5% as the MeOH: ESB mole ratio increases with an increase in agitation speed to 800 rpm. The result confirmed the essence of using excess MeOH which must be optimized in view of the phase [14]. The increase in the % yield of SBD is insignificant as the MeOH: ESB mole ratio increases from 4:1 to 8:1 at an agitation speed of 200 rpm. This is due to incomplete reaction with lower mixing intensity, because distributions of oil are not as uniform as that of higher

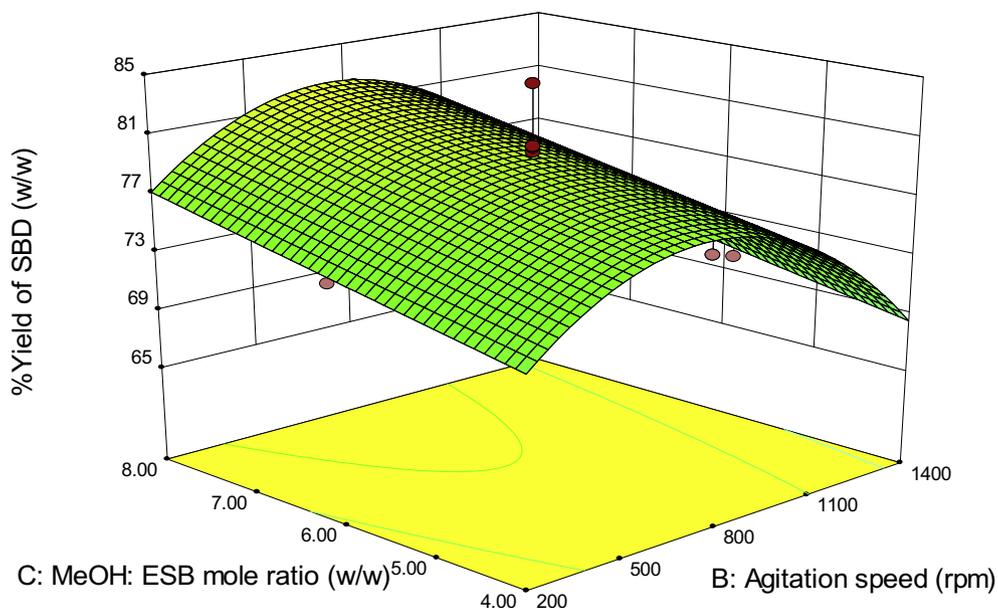


Figure 10 Effect of Agitation speed and MeOH: ESB mole ratio on %Yield of SBD.

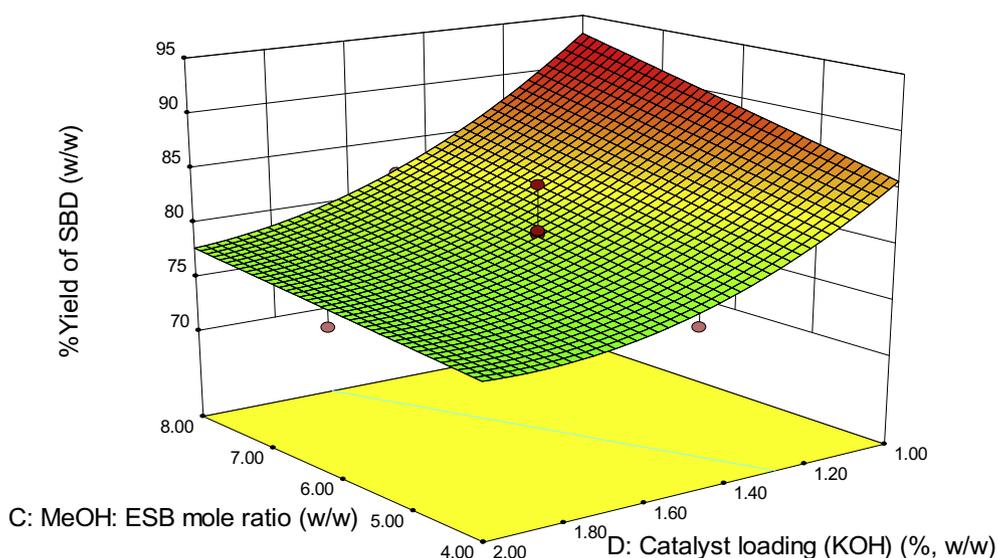


Figure 11 Effect of MeOH: ESB mole ratio and Catalyst loading on %Yield of SBD.

mixing speed [27]. The combined effect of MeOH: ESB ratio and catalyst loading on %yield of SBD at a constant temperature of 50°C and agitation speed of 800 rpm are shown in Fig. 11. The %yield of SBD was 93% when MeOH: ESB mole ratio of 8:1 was used with a catalyst loading of 1% (w/w).

3.5. Effect of interaction of catalyst loading with agitation speed on %yield of SBD

The combined effect of agitation speed and catalyst loading on %yield of SBD at a temperature of 50°C and MeOH: ESB mole ratio of 6:1 (w/w) is shown in Fig. 12. It can be deduced from the figure that the yield of SBD increases with increasing the agitation speed from 200 to 800 rpm and low catalyst load-

ing of 1% (w/w). A further increase in agitation speed to 1400 rpm with an increase in catalyst loading to 2% (w/w) decreases the %yield of SBD. This showed that the increase in the %yield of SBD depends on the quantity of catalyst loading in the reaction because at catalyst loading (KOH) of 1% (w/w), %yield of SBD was the highest (90%). When catalyst loading exceeded 1.5% (w/w), the reaction mixture solidified from the formation of soap. The results in this study are similar to that reported in the literature [18].

3.6. Optimization analysis

The regression Eq. (4) was solved using the design expert and the predicted optimal values for the variables were obtained

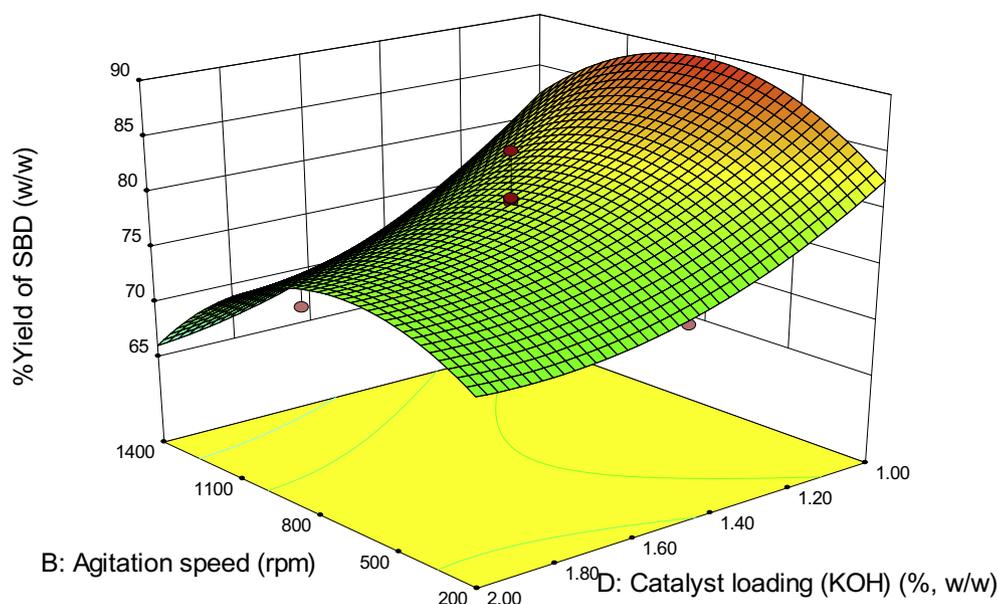


Figure 12 Effect of Agitation speed and Catalyst loading on %Yield of SBD.

Table 10 Optimal Parameters for Transesterification of ESB.

Parameters	Optimum Level	Low Level	High Level
A Temperature (°C)	40.19	40.00	60.00
B Agitation Speed (rpm)	807.98	200.00	1400.00
C Mole Ratio (w/w)	7.25	4.00	8.00
D Catalyst (KOH, w/w)	1.00	1.0	2.0
<i>% Yield of SBD</i>			
Predicted Result	93.39	55.82	91.86
Empirical Result	92.16		
Percentage error	1.32		

for transesterification of ESB for SBD production as: temperature of 40.19°C, agitation speed of 807.98 rpm, MeOH: ESB ratio of 7.25:1 (w/w) and catalyst loading of 1.0% (w/w) as shown in Table 10, with optimum SBD yield of 93.39%. The model predictions were validated by repeating the experiment in triplicate using the predicted optimal values. The %yield of SBD obtained was an average value of 92.16%, which is very close to the model prediction. Table 10 shows the %error of 1.32%, which is within the allowable limit of $\leq 5\%$. This result showed that the predicted result is in agreement with the experimental value.

4. Conclusion

The high FFA (6.86%) of SB was reduced to 0.26% by its pretreatment with MeOH: SB ratio of 2:1 using H_2SO_4 of 1.5% (v/v) at a temperature of 52°C and agitation speed of 200 rpm. The %yield of SBD obtained was 92.16% at a temperature of 40°C, agitation speed of 800 rpm, MeOH: ESB ratio of 7:1 using KOH of 1% (w/w). The variables considered for esterification and transesterification reactions showed a significant effect on the %FFA reduction and %yield of SBD

respectively. The model can successfully be employed in the vegetable oil process industry to reduce the FFA content of SB for various purposes. It can also be applied in the process of ESB for SBD production, thereby saving time and maximizing the yield of SBD.

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