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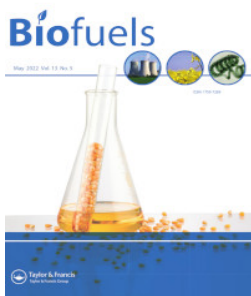


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Process optimization of KOH catalyzed biodiesel production from crude sunflower-mahua oil

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ABSTRACT

The aim of the present work is to optimize process parameters to maximize biodiesel conversion from equal proportion of mixed crude sunflower-mahua oil (CSMO) through sequential esterification-transesterification reaction using KOH as catalyst. In this study, free fatty acid (FFA) was analyzed in mixed CSMO and found to be 9.8%. So, esterification was performed using sulfuric acid as catalyst to minimize the FFA. When FFA reached 3.5% (w/w), transesterification was performed for maximum biodiesel conversion through methanolysis. Plackett–Burman design (PBD) was used to screen the significant factors to maximize biodiesel production. Then, response surface methodology (RSM) based Box–Behnken design (BBD) was employed to develop a model relating independent and dependent process parameters. Finally, generalized reduced gradient (GRG) was performed to find optimal solution for biodiesel production. The optimization results revealed that the maximum FFA conversion of 93.34% was achieved at FFA of 3.52% (w/w), molar ratio of alcohol to oil of 8.61, mass ratio of catalyst to oil of 1.45%, reaction time of 23.5 h and reaction temperature of 63.9°C, and the results were within ±1.4%. Thus, mixed CSMO could be utilized as prospective feedstock for biodiesel production.

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Mixed crude sunflower-mahua oil; biodiesel; esterification; transesterification; optimization

1. Introduction

Biodiesel is an alternative liquid transportation biofuel to conventional diesel because it improves energy security and abatement of air pollution by reducing particulate, carbon monoxide, hydrocarbon, and pollutant concentrations in diesel vehicles [1]. Over the past two decades, compressed natural gas (CNG), liquefied petroleum gas (LPG) and electricity power have emerged as energy sources for transportation. Utilizing them in vehicles requires several engine modifications and separate fuel distribution [2]. Biodiesel can be used in its pure form with little or no modifications in existing diesel engines. Biodiesel works well with new technologies such as catalysts (which can reduce the soluble fraction of diesel particulates but not the solid carbon fraction), particulate traps and exhaust gas re-circulation. Most research studies have depicted no appreciable difference between biodiesel and diesel in engine durability or in carbon deposits [3–5]. When an engine is transformed from biodiesel blend to pure diesel as fuel, carbon deposits clog the filters and leads to frequent filter replacements. Also, pure biodiesel has less energy content per gallon and affect environment [6]. Hence, biodiesel blend is a fuel for clean combustion from domestic and renewable resources. The fuel properties of fatty acid methyl ester (FAME) were comparable to EN 14214 and ASTM D6751 biodiesel standards [7].

Biodiesel can be produced from oils and fats, and the choice of feedstocks depends upon geography and cultivar. The most common feedstock of edible oils used to produce biodiesel are soybean oil, rapeseed oil and palm oil, which accounts for the bulk production of global biodiesel [8]. Other raw materials may come from non-edible sources

such as *Jatropha*, mustard, flax, and hemp. Animal fats, including sebum, lard, yellow fat, chicken fat and fish oil derivatives, may contribute to a small percentage of biodiesel production in the future, but their supply is limited and inefficient to raise animals for their fat [9–11].

Chemically, biodiesel is a mixture of alkyl esters of fatty acids. The two major factors that affect the biodiesel production are the raw material cost and the processing cost, though the commercialization of glycerol can share the cost of production with biodiesel, improving the profitability of overall process [12]. Biodiesel is easy to use, biodegradable, non-toxic, essentially free of sulphur and aromatics and provide better lubricity. The three basic ways of producing biodiesel from oils and fats are as follows [13]: (a) Direct transesterification of oils or fats catalysed by alkali or heterogeneous catalyst; (b) Esterification of oils or fats by acid catalysis followed by transesterification; and (c) Conversion of oils and fats to its fatty acids and then to biodiesel.

Biodiesel can be mixed with petro-diesel in any proportion to produce a biodiesel blend like B5 (5% biodiesel and the rest petro-diesel by volume), B10 or B20, or it can be used in a pure form. Like petro-diesel, biodiesel works with the diesel engine with auto-ignition [14]. Special storage infrastructure is not required for biodiesel blend because it can be stored as a petro-diesel. But, corrosion and contamination due to biodegradability are serious concerns in the long term storage of pure biodiesel [15]. Currently, many biodiesel production plants around the world are functioning to full capacity, and a large number are under construction or designed to meet growing global demand [16].

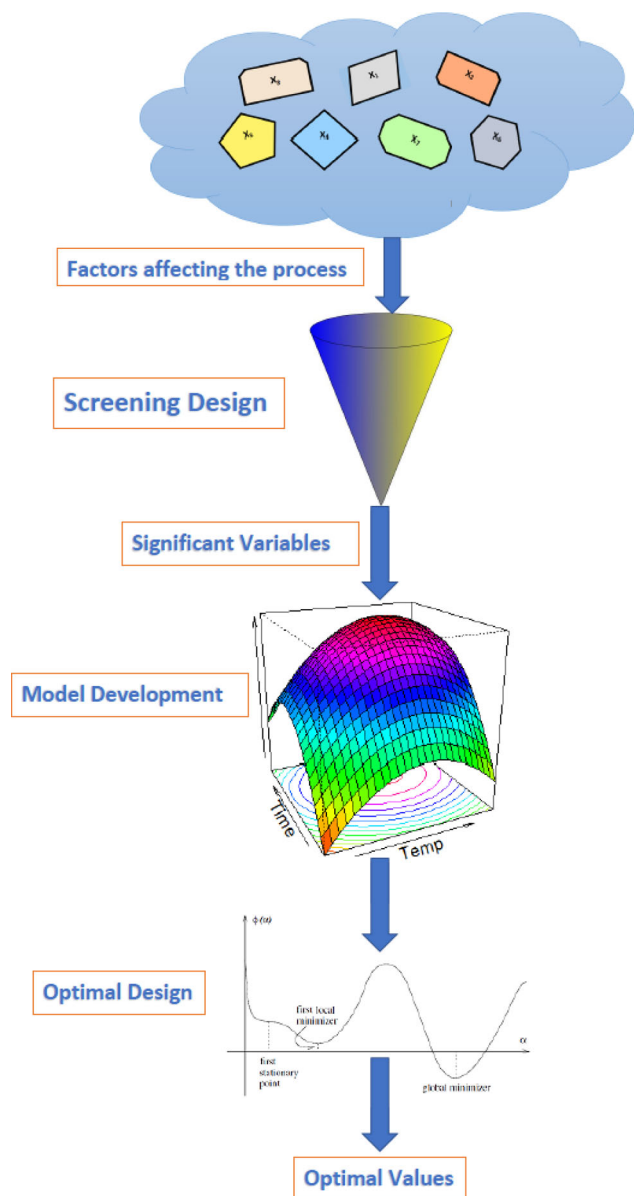


Figure 1. Screening-modelling-optimal design approach for optimization of process parameters.

Multivariant techniques are used widely since the past few years for the process optimization. The traditional method of process optimization is laborious, expensive, and mostly erroneous. Design of experiments can be performed with a smaller number of trials and minimum or no error than traditional method of experimentation. Design of experiments based on response surface methodology can be applied for process optimization through the development of mathematical model [17]. Figure 1 shows the screening-modelling-optimal design approach for optimization of process parameters.

Plackett–Burman design (PBD) is used for the screening of parameters that affect the process. Box–Behnken design (BBD) based on Response surface methodology (RSM) is three level design and slightly more efficient than other methods [18]. BBD is used to develop quadratic model relating independent and dependent variables and obtain optimal response value by generalized reduced gradient (GRG). The GRG is an iterative procedure based on a line search algorithm in which search direction and step size are calculated to achieve an optimal value [19].

Literature studies show that abundant scientific reports are available on production of biodiesel from pure edible vegetable oils [20–22], pure non-edible vegetable oils [23–26], waste vegetable oils [27–29], algal oils [30–32] and animal fats [33, 34]. But, only limited literature is available on biodiesel production from crude vegetable oils [35, 36], recycled fats [37, 38], and mixed oils [39–42]. From the analysis of literature, limited research has been carried out on biodiesel production from mixed oils and process optimization using screening-modelling-optimal design approach to maximize FFA conversion during transesterification. The studies on biodiesel production from single oils is vast than mixed oils. Mixed oils as feedstock offer many advantages such as reduced viscosity and flow properties. Hence, biodiesel production from mixed oil is state-of-the-art work. So, the present aimed to optimize process parameters to maximize biodiesel conversion from equal proportion of mixed crude sunflower-mahua oil (CSMO) through sequential esterification-transesterification reaction using KOH as catalyst by employing screening, modelling and optimal designs using Plackett–Burman, Box–Behnken and generalized reduced gradient methods.

2. Materials and methods

2.1. Materials

Crude sunflower and mahua oils were generously provided by the cold pressed oil manufacturer in Tamil Nadu, India. All the chemicals used in the work are of analytical grade and the products of VWR International. Double distilled water was used in this study. All the chemicals and reagents were used as it is unless otherwise specified.

2.2. Esterification of mixed CSMO

The mixed crude sunflower-mahua oil was prepared by mixing 1 L each of crude sunflower and mahua oils. The esterification process of mixed CSMO was performed with alcohol to oil molar ratio of 30:1 and sulphuric acid concentration of 3% (w/w) based on oil at 60 °C for 1 h. The molecular weight of the mixed CSMO was calculated based on molecular weight of the fatty acids. The CSO was added in the reaction flask fitted with reflux condenser, magnetic stirrer, and thermometer, and heated. When the temperature reached 60 °C, the alcohol-acid catalyst mixture was added to the oil and the final mixture was stirred for 1 h. The mixture was settled overnight, and the two phases were obtained. The upper phase consists of the alcohol-water-acid mixture and the lower phase consists of esterified and unreacted CSO. The lower phase was subjected to heating at 105 °C for an hour to remove excess alcohol-water and then filtered. The FFA of the esterified oil mixture was measured following the below procedure [43]:

Standard solvent was prepared by mixing 25 mL diethyl ether and 25 mL 95% ethanol and titrated against 0.1 N KOH using 1 mL of 1% phenolphthalein solution as an indicator. 5 g of oil was dissolved in 50 mL of standard solvent in a 250 mL Erlenmeyer flask. The contents are titrated against 0.1 N KOH using few drops of phenolphthalein as an indicator. The end point is the appearance of pink color that lasts for 15 s. Then, FFA was calculated using the

Equation (1) as below:

$$\text{Free fatty acid value (\%)} = \frac{\text{Titre value} \times \text{Normality of KOH} \times 28.05}{\text{Mass of oil}} \quad (1)$$

2.3. Transesterification of esterified mixed CSMO

The transesterification process and laboratory apparatus were the same as those of esterification experiments except for catalyst. Figure 2 shows the feedstock, transesterification process and final product. The reaction temperature was fixed for specified reaction time. After the transesterification reaction, the glycerine layer was separated in a separating funnel and the ester layer was washed with hot water. After washing process, the methyl ester was subjected to heating at 105 °C to remove excess alcohol and water, and then filtered. The produced methyl esters were analyzed for FFA. Finally, FFA of oil and biodiesel were measured and the percentage FFA conversion was calculated using the Equation (2) as given below [44]:

$$\% \text{ FFA conversion} = \frac{(\text{FFA in oil} - \text{FFA in biodiesel})}{\text{FFA in oil}} \times 100 \quad (2)$$

2.4. Screening of process parameters using Plackett–Burman design

The factors affecting transesterification are feedstock quality, molar ratio of methanol to oil ratio (X_1), mass ratio of KOH to oil (X_3), agitation speed (X_5), reaction time (X_6) and temperature (X_7). Typically, FFA (X_2) and moisture content (X_4) of oil decide the quality of feedstock. The levels for each variable were selected from preliminary trials. Plackett–Burman design (PBD) allows the evaluation of (N-1) variables by N experiments where N must be a multiple of 4 starting from 8. In this study, eight experiments were performed for screening of seven process variables. PBD analysis was performed following the procedure provided in Ref. [45]. Mean square was calculated to determine the significance of variables represented by the Equation (3):

$$\text{Mean square} = \frac{(\sum(+1) - \sum(-1))^2}{N} \quad (3)$$

where $\sum(+1)$ and $\sum(-1)$ are the sum of higher and lower levels, respectively, and N is number of experiments.

2.5. RSM modelling using BBD

From the PBD, the significant variables were screened to be molar ratio of alcohol to oil, mass ratio of catalyst to oil, reaction time and temperature for the maximum percentage removal of FFA. Box–Behnken design (BBD) was selected in the study because it requires lesser experiments. The number of experiments required by BBD is $2f(f-1) + CP$ where f is the number of input factors and CP is the number of centre points. For four factors and three centre points, the number of experiments required by BBD is 27. In BBD, two factors are varied at a time which leads to the study of interaction effect among the factors. The coded values are calculated using the Equation (4):

$$x_c = \frac{x_a - \bar{x}}{\Delta x} \quad (4)$$

where, x_c is the coded value, x_a is the actual value, \bar{x} is the mean value and Δx is the difference between values. A general quadratic equation that relates dependent and independent factors are given as in Equation (5),

$$Y = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_3 + \alpha_3 X_6 + \alpha_4 X_7 + \alpha_5 X_1 X_3 + \alpha_6 X_1 X_6 + \alpha_7 X_1 X_7 + \alpha_8 X_3 X_6 + \alpha_9 X_3 X_7 + \alpha_{10} X_6 X_7 + \alpha_{11} X_1^2 + \alpha_{12} X_3^2 + \alpha_{13} X_6^2 + \alpha_{14} X_7^2 \quad (5)$$

where Y is the response (% FFA conversion), X_1 is molar ratio of methanol to oil, X_3 is mass ratio of KOH to oil, X_6 is reaction time, X_7 is reaction temperature, α_0 is intercept, α_1 , α_2 , α_3 and α_4 are linear coefficients for molar ratio of methanol to oil, mass ratio of KOH to oil, reaction time and temperature, respectively, α_5 , α_6 , α_7 , α_8 , α_9 and α_{10} are interaction coefficients between molar ratio of methanol to oil and mass ratio of KOH to oil, molar ratio of methanol to oil and reaction time, molar ratio of methanol to oil and reaction temperature, mass ratio of KOH to oil and reaction time, mass ratio of KOH to oil and reaction temperature, and reaction time and temperature, respectively, and α_{11} , α_{12} , α_{13} and α_{14} are quadratic coefficients for molar ratio of methanol to oil, mass ratio of KOH to oil, reaction time and temperature, respectively.

Design-Expert® version 13.0.4.0 (64-bit) was used to perform BBD analysis for the model. Coefficients were determined by the principle of least squares, which states that the sum of the square of residuals is zero. For 27 experiments, if Equation (5) is represented in the form of a matrix, then Equation (6) is obtained as below:

$$AX = B \quad (6)$$

where A is input value matrix, X is coefficient matrix, and B is output value matrix. The coefficient matrix X was calculated by using Equation (7).

$$X = (A^T A)^{-1} \cdot (A^T B) \quad (7)$$

After finding the coefficients, the model terms were tested for statistical significance using p-value, which should be <0.05. Three-dimensional surface plots were plotted to study the interaction effects between the input factors on the response. The variation between experimental and predicted values was analysed using residual and square of residual. Residual and square of residual should be close to zero [46, 47].

2.6. Optimization using generalized reduced gradient (GRG)

The reduced gradient algorithm prevents the usage of penalty parameters by searching along curves where optimal solutions approach closer to the feasible set. Essentially, the method utilizes the equality constraints to eliminate a subset of the variables in the second version of the nonlinear programming formulation, reducing the original problem to a bound-constrained problem in the space of the remaining variables [48]. The GRG algorithm was performed in Solver, an add-in program of Microsoft Excel 2016.



Figure 2. Experimental setup: (a) Mixed crude sunflower-mahua oil; (b) Experimental setup and (c) Biodiesel and glycerol in separating funnel.

3. Results and discussion

3.1. Esterification and transesterification of mixed CSMO

The FFA was analyzed in mixed CSMO and found to be 9.8%. So, esterification was performed using sulfuric acid as catalyst to minimize the FFA. When FFA reached 3.5% (w/w), transesterification was performed for maximum FFA conversion through methanolysis. Also, the average molecular weight of the mixed CSMO was found to be 850 g/mol according to the fatty acid composition for transesterification reaction.

3.2. Screening of process parameters using Plackett–Burman design

Methanol to oil ratio (X_1), FFA of feedstock (X_2), mass ratio of KOH to oil (X_3), moisture content of oil (X_4), agitation speed (X_5), reaction time (X_6) and temperature (X_7) were the process variables selected for screening the transesterification of mixed CSMO. Table 1 shows the PBD analysis of experiments. Based on the PBD analysis, factor with highest mean square secured rank 1 and so on. Hence, from the analysis and subsequent ranking of variables, it was found that molar ratio of alcohol to oil, mass ratio of catalyst to oil, reaction time and temperature were ranked superior to FFA and moisture content of oil, agitation speed.

3.3. RSM modelling using BBD

According to the principle of BBD, 27 experiments were performed with 4 input factors (molar ratio of alcohol to oil (X_1), mass ratio of catalyst to oil (X_3), reaction time (X_6) and temperature (X_7)) and 3 centre points (Table 2). In the present study, percentage conversion of FFA is the response for transesterification of mixed CSMO.

The quadratic equation relating input factors and responses is given below in Equation (8):

$$\begin{aligned}
 Y = & -339.97 + 12.79 * X_1 + 74.42 * X_3 + 4.74 * X_6 \\
 & + 8.41 * X_7 - 0.14 * X_1 * X_3 - 0.006 * X_1 * X_6 \\
 & - 0.006 * X_1 * X_7 - 0.018 * X_3 * X_6 + 0.034 * X_3 * X_7 \\
 & + 0.0009 * X_6 * X_7 - 0.7 * X_1^2 - 25.92 * X_3^2 - 0.1 * X_6^2 \\
 & - 0.066 * X_7^2
 \end{aligned} \quad (8)$$

where, Y is % FFA conversion. The equation, in terms of actual factors, can be used to make predictions about the response for given levels of each factor.

Table 3 shows the ANOVA table for quadratic model relating input factors and response in biodiesel production from CSMO. ANOVA reveals that the model and the model terms to be significant with F-value of 918.11 and p -value < 0.05 at 95% confidence interval. The p -value of lack of fit of 0.5487, which is greater than 0.05, also reveals the statistical significance of model.

Three-dimensional surface plots are used to study the interaction effects between molar ratio of methanol to oil, mass ratio of KOH to oil, reaction time and temperature on % FFA conversion for transesterification of mixed CSMO [26]. Figure 3(a) depicts the effect of molar ratio of methanol to oil and mass ratio of KOH to oil on FFA conversion at the centre reaction time and temperature of 24 h and 65 °C, respectively. It was shown that at molar ratio of alcohol to oil of 6 and mass ratio of KOH to oil of 1, the FFA conversion was 81.95%. When molar ratio of methanol to oil and mass ratio of KOH to oil increased to 9 and 1.5%, respectively, the FFA conversion was increased to 92.05%. When molar ratio of methanol to oil and mass ratio of KOH to oil were further increased to 12 and 2%, respectively, the FFA conversion decreased to 76.18%.

Figure 3(b) illustrates the effect of molar ratio of methanol to oil and reaction time on FFA conversion at the centre mass ratio of KOH to oil and temperature of 1.5% and 65 °C, respectively. It was shown that at molar ratio of alcohol to oil of 6 and reaction time of 16 h, the FFA conversion was 82.14%. When molar ratio of methanol to oil and reaction time increased to 9 and 24 h, respectively, the FFA conversion was increased to 92.05%. When molar ratio of methanol to oil and reaction time were further increased to 12 and 32 h, respectively, the FFA conversion decreased to 75.93%.

Figure 3(c) exhibits the effect of molar ratio of methanol to oil and reaction temperature on FFA conversion at the centre mass ratio of KOH to oil and reaction time of 1.5% and 24 h, respectively. It was shown that at molar ratio of alcohol to oil of 6 and reaction temperature of 60 °C, the FFA conversion was 81.94%. When molar ratio of methanol to oil and reaction temperature increased to 9 and 65 °C, respectively, the FFA conversion was increased to 92.05%.

Table 1. PBD analysis of process variables for transesterification of mixed CSMO.

Variables	Levels		Experiments								Mean square	Rank	
	Low (−1)	High (+1)	1	2	3	4	5	6	7	8			
X ₁	Molar ratio of alcohol to oil	3	12	−1	1	1	1	−1	1	−1	−1	56.2	1
X ₂	FFA of oil (%)	2.5	3.5	−1	−1	1	1	1	−1	1	−1	1.12	5
X ₃	Mass ratio of catalyst to oil (%)	1	2	1	−1	−1	1	1	1	−1	−1	32	2
X ₄	Moisture content of oil (%)	0.5	2	−1	1	−1	−1	1	1	1	−1	1.12	5
X ₅	Agitation speed (rpm)	50	150	1	−1	1	−1	−1	1	1	−1	0.02	6
X ₆	Reaction time (h)	16	32	1	1	−1	1	−1	−1	1	−1	15.7	3
X ₇	Reaction temperature (°C)	60	70	1	1	1	−1	1	−1	−1	−1	9.2	4
% FFA conversion				78.6	81.2	83	85	86.8	89.3	90.8	85.4		

Table 2. Experimental design for BBD of transesterification of mixed CSMO.

Variables	Unit	Levels						Residual	Square of residual
		Low		Centre		High			
		Coded	Actual	Coded	Actual	Coded	Actual		
X ₁	Molar ratio of alcohol to oil	−1	6	0	9	+1	12		
X ₃	Mass ratio of catalyst to oil	−1	1	0	1.5	+1	2		
X ₆	Reaction time	−1	16	0	24	+1	32		
X ₇	Reaction temperature	−1	60	0	65	+1	70		
Molar ratio of alcohol to oil	Mass ratio of catalyst to oil	Reaction time	Reaction temperature	% FFA conversion					
X ₁	X ₃ (%)	X ₆ (h)	X ₇ (°C)	Experimental	Predicted				
12	1	24	65	79.12	79.34	−0.22	0.0484		
6	2	24	65	79.85	79.57	0.28	0.0784		
6	1.5	24	55	81.94	82.01	−0.07	0.0049		
9	1.5	24	65	92.05	92	0.05	0.0025		
9	1	16	65	81.69	81.85	−0.16	0.0256		
9	1.5	32	55	78.79	78.78	0.01	0.0001		
9	2	16	65	78.95	79.16	−0.21	0.0441		
9	1.5	24	65	91.78	92	−0.22	0.0484		
9	1	24	55	82.06	82.03	0.03	0.0009		
9	2	24	55	78.63	78.86	−0.23	0.0529		
12	1.5	16	65	79.42	79.33	0.09	0.0081		
12	1.5	24	55	79.38	79.3	0.08	0.0064		
6	1.5	32	65	79.26	79.33	−0.07	0.0049		
9	1.5	32	75	75.75	75.86	−0.11	0.0121		
6	1.5	24	75	79.13	79.3	−0.17	0.0289		
12	2	24	65	76.18	76.08	0.1	0.01		
9	1.5	16	75	78.84	78.78	0.06	0.0036		
6	1	24	65	81.95	81.98	−0.03	0.0009		
9	2	32	65	76.03	75.95	0.08	0.0064		
6	1.5	16	65	82.14	82.09	0.05	0.0025		
12	1.5	32	65	75.93	75.96	−0.03	0.0009		
12	1.5	24	75	75.86	75.88	−0.02	0.0004		
9	1	32	65	79.06	78.93	0.13	0.0169		
9	1.5	16	55	82.16	81.99	0.17	0.0289		
9	2	24	75	76.12	76.13	−0.01	1E−04		
9	1.5	24	65	92.16	92	0.16	0.0256		
9	1	24	75	78.87	78.63	0.24	0.0576		

Residual = Experimental − Predicted values.

Table 3. ANOVA for quadratic model relating input factors and response in biodiesel production from CSMO.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	556.82	14	39.77	918.11	<0.0001	significant
X ₁	28.15	1	28.15	649.86	<0.0001	
X ₃	28.15	1	28.15	649.86	<0.0001	
X ₆	24.06	1	24.06	555.28	<0.0001	
X ₇	28.18	1	28.18	650.57	<0.0001	
X ₁ X ₃	0.0930	1	0.0930	2.15	0.01685	
X ₁ X ₆	0.1764	1	0.1764	4.07	0.00665	
X ₁ X ₇	0.1260	1	0.1260	2.91	0.01138	
X ₃ X ₆	0.0210	1	0.0210	0.4853	0.04993	
X ₃ X ₇	0.0196	1	0.0196	0.4524	0.05139	
X ₆ X ₇	0.1156	1	0.1156	2.67	0.01283	
X ₁ ²	209.98	1	209.98	4847.06	<0.0001	
X ₃ ²	228.26	1	228.26	5269.16	<0.0001	
X ₆ ²	224.01	1	224.01	5170.95	<0.0001	
X ₇ ²	232.55	1	232.55	5368.28	<0.0001	
Residual	0.5198	12	0.0433			
Lack of fit	0.4434	10	0.0443	1.16	0.5487	not significant
Pure error	0.0765	2	0.0382			
Cor total	557.34	26				

When molar ratio of methanol to oil and reaction temperature were further increased to 12 and 70 °C, respectively, the FFA conversion decreased to 79.13%.

Figure 3(d) illustrates the effect of mass ratio of KOH to oil and reaction time on FFA conversion at the centre molar ratio of methanol to oil and temperature of 9 and 65 °C, respectively. It was shown that at mass ratio of KOH to oil of 1% and reaction time of 16 h, the FFA conversion was 81.69%. When mass ratio of KOH to oil and reaction time increased to 1.5% and 24 h, respectively, the FFA conversion was increased to 92.05%. When mass ratio of KOH to oil and reaction time were further increased to 2% and 32 h, respectively, the FFA conversion decreased to 76.03%.

Figure 3(e) depicts the effect of mass ratio of KOH to oil and reaction temperature on FFA conversion at the centre molar ratio of methanol to oil and reaction time of 9 and 24 h, respectively. It was shown that at mass ratio of KOH to oil of 1% and reaction temperature of 60 °C, the FFA conversion was 82.06%. When mass ratio of KOH to oil and reaction temperature increased to 1.5% and 65 °C,

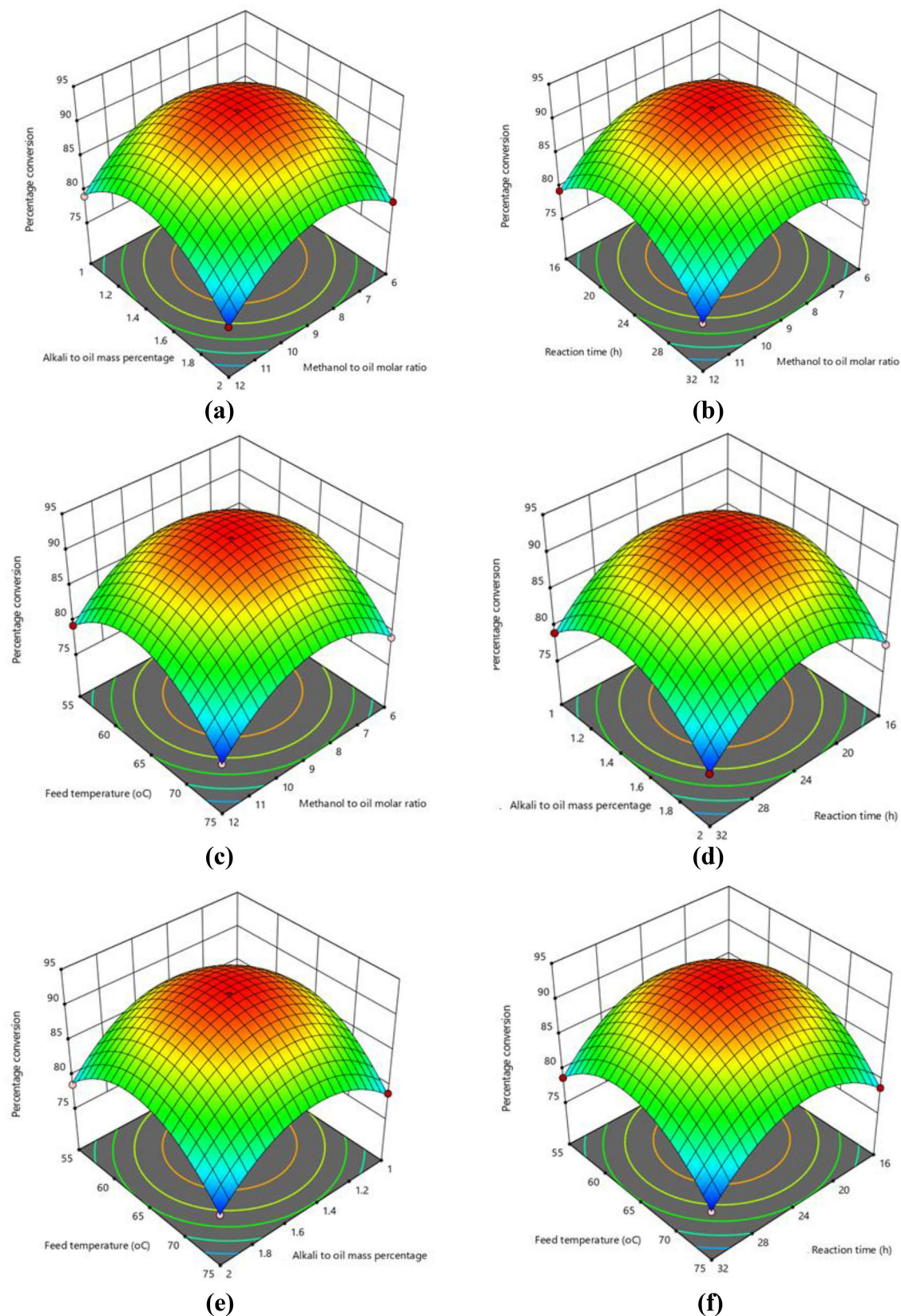


Figure 3. Three-dimensional surface plots showing the interaction effect of (a) molar ratio of methanol to oil and mass ratio of KOH to oil, (b) molar ratio of methanol to oil and reaction time, (c) molar ratio of methanol to oil and reaction temperature, (d) mass ratio of KOH to oil and reaction time, (e) mass ratio of KOH to oil and reaction temperature and (f) reaction time and temperature for transesterification of mixed CSMO.

respectively, the FFA conversion was increased to 92.05%. When mass ratio of KOH to oil and reaction temperature were further increased to 2% and 70 °C, respectively, the FFA conversion decreased to 76.12%.

Figure 3(f) exhibits the effect of reaction time and temperature on FFA conversion at the centre molar ratio of methanol to oil and mass ratio of KOH to oil of 9 and

1.5%, respectively. It was shown that at reaction time and temperature of 16 h and 60 °C, respectively, the FFA conversion was 82.16%. When reaction time and temperature increased to 24 h and 65 °C, respectively, the FFA conversion was increased to 92.05%. When reaction time and temperature were further increased to 32 h and 70 °C, respectively, the FFA conversion decreased to 75.75%.

3.3 Optimization using generalized reduced gradient (GRG):

Microsoft Excel 16.0 Answer Report				
Worksheet: GRGResponseSheet				
Report Created: 03/01/2022 06:48:34				
Result: Solver found a solution. All Constraints and optimality conditions are satisfied.				
Solver Engine				
Engine: GRG Nonlinear				
Solution Time: 0.016 Seconds.				
Iterations: 1 Subproblems: 0				
Solver Options				
Max Time Unlimited, Iterations Unlimited, Precision 0.000001, Use Automatic Scaling				
Convergence 0.0001, Population Size 100, Random Seed 0, Derivatives Forward, Require Bounds				
Max Subproblems Unlimited, Max Integer Sols Unlimited, Integer Tolerance 1%, Assume NonNegative				
Objective Cell (Max)				
Cell	Name	Original Value	Final Value	
\$E\$2	Y	93.37081066	93.37081066	
Variable Cells				
Cell	Name	Original Value	Final Value	Integer
\$A\$2	X1	8.616316575	8.616316575	Contin
\$B\$2	X3	1.445985645	1.445985645	Contin
\$C\$2	X6	23.59871212	23.59871212	Contin
\$D\$2	X7	63.85378947	63.85378947	Contin
Constraints				
NONE				

Figure 4. Spreadsheet showing the optimization of FFA conversion in transesterification of mixed CSMO.

Table 4. Validation of optimal conditions predicted by GRG.

Molar ratio of alcohol to oil	Mass ratio of catalyst to oil (%)	Reaction time (h)	Reaction temperature (°C)	% FFA conversion			
				Experimental value	Average experimental value	GRG prediction	Relative error (%)
8.61	1.45	23.5	63.9	93.36 93.25 93.41	93.34	93.37	0.03%

3.3. Optimization using generalized reduced gradient (GRG)

Figure 4 shows the response sheet obtained after running the GRG algorithm in Solver. The optimization results revealed that the maximum FFA conversion of 93.37% was achieved at FFA of 3.52% (w/w), molar ratio of alcohol to oil of 8.61, mass ratio of catalyst to oil of 1.45%, reaction time of 23.5 h and reaction temperature of 63.9 °C. The optimization was performed as an unconstrained nonlinear problem using an objective function, Equation (8). The results were attained in less than a second and single iteration, which proves the robustness and reliability of an algorithm [48].

3.4. Validation of optimum conditions

Table 4 shows the validation of maximum FFA conversion at optimum values of molar ratio of methanol to oil, mass

ratio of KOH to oil, reaction time and temperature. The optimum values obtained from the GRG were validated by performing experiments in triplicate. The relative error of 0.03% indicates the minimum variation between the experimental and predicted values [45].

4. Conclusion

The presented work has aimed to develop mathematical model for the transesterification of mixed CSMO using KOH catalyst and optimize the process parameters. Methanol to oil ratio (X_1), FFA of feedstock (X_2), mass ratio of KOH to oil (X_3), moisture content of oil (X_4), agitation speed (X_5), reaction time (X_6) and temperature (X_7) were the process variables selected for screening the transesterification of mixed CSMO. The process parameters were screened by Plackett–Burman design and found that molar ratio of methanol to oil, mass ratio of KOH to oil, reaction time and

temperature appropriate for optimization. After modelling of process variables with FFA conversion by BBD, the maximum FFA conversion of 93.34% was achieved for maximum FFA conversion at optimal FFA of 3.52% (w/w), molar ratio of alcohol to oil of 8.61, mass ratio of catalyst to oil of 1.45%, reaction time of 23.5 h and reaction temperature of 63.9 °C. The present work could be validated further by performing optimization through ANN-GA methodologies and economic analysis. Thus, mixed CSMO could be utilized as prospective feedstock for biodiesel production.

Nomenclature

Unit	Factor
-	Molar ratio of alcohol to oil
%	FFA of oil
%	Mass ratio of catalyst to oil
%	Moisture content of oil
rpm	Agitation speed
h	Reaction time
°C	Reaction temperature

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Disclosure statement

No potential competing interest was reported by the authors.

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