Effectiveness of RSM based Central Composite Design for optimization of in-situ biodiesel production process from castor seeds

K Thakkar1,3, S S Kachhawaha1,3, P Kodgire2,3, and M Keshav1
1Department of Mechanical Engineering, Pandit Deendayal Petroleum University, Gandhinagar, India
2Department of Chemical Engineering, Pandit Deendayal Petroleum University, Gandhinagar, India
3Centre of Biofuel and Bioenergy Studies (CBBS), Pandit Deendayal Petroleum University, Gandhinagar, India

Corresponding author: kartik.tphd16@sot.pdpu.ac.in, surendra.singh@sot.pdpu.ac.in

Abstract. In the present experimental study, biodiesel is made by reactive extraction (in-situ method) of castor seed. The hybrid (MW+US) apparatus was used to intensify in-situ process. Potassium Hydroxide (KOH) as catalyst and methanol as a reagent are used for the transesterification process. Response surface methodology has been applied to design the experiments. A central composite design (CCD) was adopted to examine the influence of various process parameters (MeOH:seeds ratio (v/w), catalyst loading, reaction temperature and, time) on the biodiesel yield. The optimum conditions for maximum biodiesel yield (93.2%) obtained for castor seed, are 7.47 methanol to oil ratio (v/w), 1.7% KOH catalyst loading, 317 K reaction temperature, and 1788 s reaction time. The regression equation obtained for the model having a coefficient of correlation ($R^2$), and adjusted coefficient of correlation ($R^2_{adj}$) are 0.974 and 0.951 respectively shows the goodness of fit for the model.

1. Introduction
Biodiesel is a sustainable alternative to petro-diesel derived from edible/non-edible plant oils, animal fats, and used frying oil including triglycerides. [1]. Vegetable oil feedstocks are widely available from various plant sources, and the glycerides present in the oils are suitable for the transesterification reaction used to obtain fatty acid methyl esters [2].

Biodiesel is a mixture of mono-alkyl esters of various types of fatty acids. Thus, biodiesel is made by converting fatty acid into the respective esters. In transesterification reaction, triglyceride present in vegetable oil is reacted with alcohol and get converted into a mixture of mono-alkyl esters. Conventionally, oil or animal fat is extracted from raw feedstock and the reaction is carried out between extracted oil and methanol. In other words, this method comprises three stages viz. oil-extraction, purification (degumming, deacidification, dewaxing, dehydration, dephosphorization, etc.), and transesterification. The requirement of these processing stages (except transesterification) constitutes over 70% of the total production cost of biodiesel [3]. Therefore, the reactive extraction
process (development of in-situ extraction, esterification, and transesterification) has the potential to decrease the processing cost.

The application of ultrasound for intensification of biodiesel synthesis has been reported in many studies in the last decade. It has been reported that ultrasound and cavitation have beneficial effects such as higher yield, faster kinetics, reduction in the number of process steps, etc. [4]. The ultrasound system is specified by frequency (kHz) as well as its intensity (W/cm²). Microwave irradiation, due to the direct delivery of energy to the mixture is a well-established technique to accelerate and enhance chemical reactions [5]. MW enhances the reaction speed and makes the separation process less complex compared to conventional heating [6].

PI techniques (ultrasound and microwave) have limitations which include attenuation effect in ultrasound and low penetration depth and uncontrolled heating in the microwave [7]. These limitations can be minimized by the hybrid approach and the combined effect of microwave (heat transfer barrier removal) and ultrasound (mass transfer barrier removal) lead to synergistic effects [8].

Hence, the main objective of this research was to incorporate microwave and ultrasound energy intensification simultaneously to the in-situ process of biodiesel production from castor seeds and to find favorable process conditions for maximum biodiesel yield. RSM based on the CCD procedure is applied to analyze the effects of each factor and their interaction.

2. Methodology

2.1. Materials

The freshly harvested castor seeds from the agricultural field of Gandhinagar, Gujarat were used in the current study. Methyl alcohol (CH₃OH) (≥99%, grade: analytical reagent) and the homogeneous catalyst KOH (≥85%) were procured from Merck and were used without purification. Chemicals required for gas chromatography (GC) which are n-Heptane, (purity ≥99.5%, grade: GC), and internal standard Methyl heptadecanoate (purity ≥99.5%, grade: GC) were purchased from Sigma-Aldrich dealer of Ahmedabad, India.

2.2. Identification of factors and their levels

In this study, RSM is being used. CCD has been adopted to study the effect of individuals and the interaction of various process parameters. As discussed above, RSM-CCD requires a 5-factor level, which is $-\alpha, -1, 0, 1, \alpha$. Here alpha ($\alpha$) is the distance between the axial points from the center in a CCD. After identifying the appropriate strategy of the experiments, it is required to decide various factors and their level from the literature study. For example low level, intermediate and high level. For this purpose, ‘0th’ experiments were conducted. From the literature survey, values of different levels can be estimated. In the present study, a set of 31 experiments was designed based on the CCD method which consists of 5 levels for each factor as shown in table 1.

| Table 1. Factors and levels in DOE |
|-------------------------------|
| Levels | Methanol:seeds ratio (v/w) (A) | % Catalyst (%wt oil) (B) | Temperature (K) (C) | Time (s) (D) |
| Axial Point $-\alpha$ | 1.6 | 0.5 | 313 | 600 |
| Lower Value $-1$ | 3.2 | 1.0 | 318 | 1200 |
| Intermediate Value 0 | 4.8 | 1.5 | 323 | 1800 |
| Upper Value 1 | 6.4 | 2.0 | 328 | 2400 |
| Axial Point $\alpha$ | 8.0 | 2.5 | 333 | 3000 |
2.3. Experimentation
Castor seeds in the sample size of fifty grams were ground in a household-type domestic grinder for half a minute to achieve 1.3 mm of average particle size. The slurry of seeds was preheated at the required temperature after mixing with methyl alcohol in a pre-defined ratio. Potassium methoxide (catalyst (KOH) + required amount of methyl alcohol) was added to the glass reactor of size 500 ml for the transesterification reaction to begin. The constant Ultrasonication of frequency 40 kHz and 50 W nominal power was applied along with microwave (power 0-50W) to maintain the temperature throughout the reaction. After the completion of the reaction, products with slurry were passed through Whatman filter paper (Grade 42) to separate solid medium using vacuum filtration. The excess methanol was recovered in a rotary evaporator. The resulting mixture consists of FAME (Fatty Acid Methyl Esters), glycerol, and un-reacted triglycerides were analyzed using GC-FID, and % FAME was calculated [8]. The by-product glycerol was separated gravimetrically in a separating funnel and removed. Catalyst (KOH) present in the product mixture was removed by washing three times with the distilled water. Finally, biodiesel was obtained after removing the moisture by heating up to 80 °C with stirring on a hotplate with a magnetic stirrer.

3. Results and discussion
3.1. Determination of regression equation and analysis of variance
The regression equation to determine yield (Y, %) in terms of coded factors using the least square method is given in Eq. (1).

\[
Y(\%) = 70.68 + 7.31A + 0.68B + 2.74C + 0.35D + 2.26A^2 - 4.03B^2 - 2.79C^2 - 3.85D^2 + 1.22AB - 5.32AC - 2.28AD - 0.54BC + 0.3BD - 2.81CD
\]  

(1)

The regression equation consists of variables of the predictors viz. methanol:seeds ratio (v/w) (A), catalyst amount (B, % wt.), reaction temperature (C, °C), reaction time (D, min) respectively. The values of \( R^2 \) and \( R^2_{\text{adj}} \) were calculated to be 97.4% and 95.1% respectively which are considered satisfactory. Predicted yield along with experimentally calculated yield of biodiesel (%) obtained through regression equation (Eq. (1)) is given in table 2. It can be observed from table 2 that, maximum experimental biodiesel yield of 91.33% is obtained for experiment no. 28 in which methanol to seed ratio (v/w) is 8.0, catalyst amount is 1.5% (w/w), the reaction temperature is 323 K, and reaction time 1800 s. The predicted biodiesel yield for the same reaction conditions is 94.34%. The minimum experimental biodiesel yield that has been obtained out of performed experiments as given in table 2 is 41.63% for the experimental run 20. The reaction conditions for the observed minimum biodiesel yield are 3.2 methanol to seed ratio (v/w), 1% catalyst amount (w/w), 318 K reaction temperature, and 1200 s reaction time. The reaction conditions corresponding to the minimum and maximum biodiesel yield are specified by the bold letters in table 2.

It is easy to follow from table 2 that, the chosen reaction parameters have significant effects on the biodiesel yield. However, the significance of each reaction parameter can be studied using analysis of variance (ANOVA) as shown in table 3. The ANOVA for the quadratic regression model is carried out using a 95% confidence interval and with a significance level of 0.05. The P-value < 0.05 demonstrates high significance with a 95% of the confidence interval in predicting the yield values and the suitability of the developed regression model as given in table 3. The “lack of fit” parameter is not significant with a p-value higher than 0.05 as can be observed from table 3 which indicates the goodness of fit of the model. The plot of actual yield vs. predicted yield (figure 1) also justifies the goodness of fit of the model.
Table 2. Experimental and predicted values of the yield.

| No. | Methanol:seeds ratio (v/w) | A | Catalyst amount (wt %) | B | C | Reaction Temp. (K) | D | Reaction time (s) | Experimental Yield (%) | Predicted Yield (%) |
|-----|---------------------------|---|------------------------|---|---|-------------------|---|-------------------|-----------------------|---------------------|
| 1   | 3.2                       | 2 |                        | 318 | 2400 | 53.51             | 52.66 |
| 2   | 4.8                       | 1.5 |                      | 323 | 3000 | 54.98             | 55.99 |
| 3   | 3.2                       | 2 |                        | 328 | 2400 | 62.72             | 62.06 |
| 4   | 4.8                       | 1.5 |                      | 323 | 1800 | 70.25             | 70.68 |
| 5   | 6.4                       | 2 |                        | 328 | 1200 | 74.92             | 72.80 |
| 6   | 6.4                       | 1 |                        | 328 | 1200 | 71.14             | 70.68 |
| 7   | 6.4                       | 2 |                        | 328 | 2400 | 65.37             | 63.93 |
| 8   | 4.8                       | 1.5 |                      | 323 | 1800 | 75.38             | 70.68 |
| 9   | 6.4                       | 1 |                        | 318 | 1200 | 69.4              | 69.13 |
| 10  | 6.4                       | 1 |                        | 318 | 2400 | 71.38             | 70.30 |
| 11  | 4.8                       | 1.5 |                      | 323 | 1800 | 70.24             | 70.68 |
| 12  | 4.8                       | 0.5 |                      | 323 | 1800 | 54.2              | 53.21 |
| 13  | 1.6                       | 1.5 |                      | 323 | 1800 | 65.89             | 65.12 |
| 14  | 6.4                       | 2 |                        | 318 | 1200 | 74.81             | 73.42 |
| 15  | 4.8                       | 1.5 |                      | 333 | 1800 | 63.77             | 65.00 |
| 16  | 4.8                       | 1.5 |                      | 323 | 600  | 53.34             | 54.57 |
| 17  | 3.2                       | 1 |                        | 328 | 1200 | 64.24             | 64.59 |
| 18  | 4.8                       | 1.5 |                      | 323 | 1800 | 73.93             | 70.68 |
| 19  | 6.4                       | 1 |                        | 328 | 2400 | 60.83             | 60.61 |
| 20  | 3.2                       | 1 |                        | 318 | 1200 | **41.63**         | **41.77** |
| 21  | 4.8                       | 1.5 |                      | 323 | 1800 | 69.02             | 70.68 |
| 22  | 3.2                       | 1 |                        | 328 | 2400 | 63.54             | 63.63 |
| 23  | 4.8                       | 1.5 |                      | 323 | 1800 | 67.92             | 70.68 |
| 24  | 4.8                       | 1.5 |                      | 313 | 1800 | 53.02             | 54.04 |
| 25  | 3.2                       | 2 |                        | 328 | 1200 | 62.04             | 61.81 |
| 26  | 6.4                       | 2 |                        | 318 | 2400 | 77.06             | 75.79 |
| 27  | 3.2                       | 2 |                        | 318 | 1200 | 41.88             | 41.17 |
| 28  | 8.0                       | 1.5 |                      | 323 | 1800 | **91.33**         | **94.34** |
| 29  | 4.8                       | 1.5 |                      | 323 | 1800 | 68.01             | 70.68 |
| 30  | 4.8                       | 2.5 |                      | 323 | 1800 | 52.69             | 55.92 |
| 31  | 3.2                       | 1 |                        | 318 | 2400 | 50.87             | 52.06 |
Table 3. Analysis of Variance (ANOVA).

| Source | DF | Adj SS | Adj MS | F-Value | P-Value | Remark |
|--------|----|--------|--------|---------|---------|--------|
| Regression | 14 | 3391.2 | 242.23 | 42.29 | 0 | S |
| A | 1 | 1281.18 | 1281.18 | 223.7 | 0 | S |
| B | 1 | 11.06 | 11.06 | 1.93 | 0.184 | |
| C | 1 | 180.15 | 180.15 | 31.46 | 0 | S |
| D | 1 | 3.01 | 3.01 | 0.53 | 0.479 | |
| A² | 1 | 146.5 | 146.5 | 25.58 | 0 | S |
| B² | 1 | 463.87 | 463.87 | 80.99 | 0 | S |
| C² | 1 | 222.6 | 222.6 | 38.87 | 0 | S |
| D² | 1 | 423.73 | 423.73 | 73.99 | 0 | S |
| AB | 1 | 23.92 | 23.92 | 4.18 | 0.058 | |
| AC | 1 | 452.07 | 452.07 | 78.93 | 0 | S |
| AD | 1 | 83.18 | 83.18 | 14.52 | 0.002 | S |
| BC | 1 | 4.73 | 4.73 | 0.83 | 0.377 | |
| BD | 1 | 1.44 | 1.44 | 0.25 | 0.623 | |
| CD | 1 | 126.41 | 126.41 | 22.07 | 0 | S |
| Error | 16 | 91.63 | 5.73 | | | |
| Lack-of-Fit | 10 | 41.12 | 4.11 | 0.49 | 0.849 | |
| Pure Error | 6 | 50.51 | 8.42 | | | |
| Total | 30 | 3482.84 | | | | |

[*S* represents significant terms in regression equation]

Figure 2 shows the standardized effect in the Pareto chart and it is also noticeable that linear terms B and D are insignificant while B² and D² are significant indicating dominant quadratic effect over linear effect which is also observable from the ANOVA (table 3) and regression equation coefficients. The most significant term affecting the conversion of biodiesel is methanol to seeds ratio (v/w) (A), while interaction terms BC and BD are insignificant as shown in figure 2.
3.2. Main and interaction effects of reaction parameters

Figure 3 shows the main effects of the four factors on biodiesel yield as predicted with a 95% confidence interval. From the trend of methanol:seeds (v/w) ratio (A), it can be followed that there is an increase in biodiesel yield with an increase in A up to upper level (coded level 1 and un-coded level 8.0), however, increase in A above 7.47 (v/w) is not economically feasible. It can also be observed that variation in catalyst loading (B) has the curvilinear effect on biodiesel yield (Y) and maximum biodiesel yield is predicted around mid-level which is also similar for other factors (C and D). With an increase in temperature (C) there is an increase in biodiesel yield up-to around 318 K, beyond 318 K there is a slow decrease in biodiesel yield with an increase in temperature. Similarly, the effect of reaction time (D) on conversion (%) is also observed to be significant with its steeper slope up to midlevel. The conversion increases significantly with an increase in reaction time (D) up to midlevel, however, there is a reduction in conversion when reaction time is increased beyond the mid-level of 1800 s.

The interaction effect of methanol:seeds ratio (v/w) and reaction temperature on biodiesel yield can be observed in figure 4. At higher methanol:seeds ratio (v/w) with a decrease in reaction temperature, an increase in the biodiesel yield is observed. Moreover, maximum biodiesel yield is obtained when the volume of methanol per unit weight of castor seeds is higher (more than the intermediate level range) due to increased oil extraction. An increase in temperature above 313 K can lead to partial evaporation of methanol which causes less solvent contact for biomass resulting in decreased oil extraction even for higher MeOH:seeds ratio (v/w) as depicted in figure 4. Similarly, figure 5 shows the interaction effect of MeOH:seeds ratio (v/w) and reaction time. It is easy to conclude from figure 5 that, if the MeOH:seeds ratio (v/w) is sufficiently high (above 6.0 v/w), a relatively higher biodiesel yield can be achieved in less reaction time.

The yield was found to be enhanced with an increase in reaction time (D) and reaction temperature (C) up to a mid-level limit. It can be concluded that increasing reaction temperature towards the boiling point of methanol inhibits the reaction. However, as shown in figure 6 that there is less penalty on biodiesel yield as a result of higher temperature if the reaction is carried out for a comparatively shorter time. Exposure to a higher temperature for a longer duration of time can lead to methanol evaporation causing a reduction in yield.

Figure 2. Pareto chart showing the significance of regression terms.
Figure 3. Main effects of factors.

Figure 4. Interaction effects of MeOH:seeds ratio (v/w) and reaction temperature.

Figure 5. Interaction effects of MeOH:seeds ratio (v/w) and reaction time.
3.3. Optimization of reaction conditions

Process optimization for maximum yield was done using State Ease Design Expert (version 10) using desirability function approach maximum desirability value of 0.883 was achieved as given in figure 7). Maximum biodiesel yield of 93.2% yield was predicted for factor level combinations of 7.47 MeOH:seeds ratio (v/w) (coded value=1.67), 1.7% (%wt.) catalyst loading (coded value=0.41), 317 K temperature (coded value= -1.13) and 1788 s of reaction time (coded value=-0.02). Maximum experimental biodiesel yield of 93.5± 0.76 % was obtained at the optimum reaction conditions which is similar to the predicted biodiesel yield calculated using the regression model.

3.4. Prediction of biodiesel yield using an extreme learning machine

In the experiment, four parameters have been taken which affect the biodiesel yield. They are MeOH:seeds ratio (v/w) (A), catalyst amount (%wt. oil) (B), reaction temperature (K) (C) and reaction time (s) (D). By using the CCD DoE technique, 31 experimental combinations have been generated and second-order RSM has been fitted as given in Eq. (1).

Further, using the given experimental results, an Extreme learning machine (ELM) has been fitted. ELM is single-layered feedforward neural network (SLFN) with activation function of hidden layer defined by radial basis network and parameters of the hidden layer initialized by random distribution. The output function of the ELM network by L^{th} layer is given by
\[ f_L = \sum_{i=1}^{l} \beta_i G(w_i, b_i, x), x \in \mathbb{R}^n \]  

(3)

Where \( w_i \) and \( b_i \) are the learning parameters of the hidden layer and \( \beta_i \) is the parameter relating the output of hidden nodes with output function. The function \( G(w_i, b_i, x) \) is the output of the \( i \)th hidden node for the input value \( x \). This function is the radial basis function (RBF) network where the weights are initialized randomly. Here, in the current study, the uniform distribution has been used for initializing the weights of the hidden layer of SLFN. The unknown coefficients, \( \beta_i \) are estimated by using Moore-Penrose pseudoinverse of the design matrix formed by initialized values of hidden node parameters and given values of input variables. It is given by

\[ \beta_i = (D^T D)^{-1} D^T f_L \]  

(4)

Here, 208 hidden nodes are chosen, and uniform distribution of parameters associated with them.

Table 4. Experimental results and predicted values by different data-driven models.

| Run No. | Experimental Yield% | RSM     | ELM     |
|---------|----------------------|---------|---------|
| 1       | 53.51                | 52.66   | 53.51   |
| 2       | 54.98                | 55.99   | 54.98   |
| 3       | 62.72                | 62.06   | 62.72   |
| 4       | 70.25                | 70.68   | 70.68   |
| 5       | 74.92                | 72.80   | 74.92   |
| 6       | 71.14                | 70.68   | 71.14   |
| 7       | 65.37                | 63.93   | 65.37   |
| 8       | 75.38                | 70.68   | 70.68   |
| 9       | 69.4                 | 69.13   | 69.4    |
| 10      | 71.38                | 70.30   | 71.38   |
| 11      | 70.24                | 70.68   | 70.68   |
| 12      | 54.20                | 53.21   | 54.20   |
| 13      | 65.89                | 65.12   | 65.89   |
| 14      | 74.81                | 73.42   | 74.81   |
| 15      | 63.77                | 65.00   | 63.77   |
| 16      | 53.34                | 54.57   | 53.34   |
| 17      | 64.24                | 64.59   | 64.24   |
| 18      | 73.93                | 70.68   | 70.68   |
| 19      | 60.83                | 60.61   | 60.83   |
| 20      | 41.63                | 41.77   | 41.63   |
| 21      | 69.02                | 70.68   | 70.68   |
| 22      | 63.54                | 63.63   | 63.54   |
| 23      | 67.92                | 70.68   | 70.68   |
| 24      | 53.02                | 54.04   | 53.02   |
| 25      | 62.04                | 61.81   | 62.04   |
| 26      | 77.06                | 75.79   | 77.06   |
| 27      | 41.88                | 41.17   | 41.88   |
| 28      | 91.33                | 94.34   | 91.33   |
| 29      | 68.01                | 70.68   | 70.68   |
| 30      | 52.69                | 55.92   | 52.69   |
| 31      | 50.87                | 52.06   | 50.87   |
Table 4 shows the experimental yield and its comparison with the predicted yield obtained through RSM and ELM. It also compares the yield predicted by RSM, Improved RSM, and ELM. Table 5 compares the performance of the fitted model using various statistical parameters. Both the models are fitting the experimental yield data with less value of error. The mean average percentage error (MAPE) is smaller in ELM compared to RSM. However, all other indicators are comparatively better for RSM than ELM.

Table 5. Comparison of different fitted data-driven models.

| Statistical Parameters | Fitted models→ | RSM | ELM |
|------------------------|----------------|-----|-----|
| R²                     |                | 0.9740 | 0.9852 |
| MSE                    |                | 1.6300 | 2.9571 |
| RMSE                   |                | 1.2768 | 1.7196 |
| SEP                    |                | 1.9896 | 2.6798 |
| Adj-R²                 |                | 0.9510 | -    |
| Correlation coefficient, R |            | 0.9927 | 0.9867 |
| MAPE                   |                | 0.0814 | 0.0319 |

4. Conclusions

The current study successfully determined optimum reaction conditions for the in-situ transesterification reaction of castor seeds intensified by hybrid energy (ultrasound and microwave) using RSM coupled with CCD. Moreover, the RSM model is also compared with the ELM, and both models are found to be accurate in predicting biodiesel yield. However, higher R² and R²_adj values of the RSM model show its fitness for the present application of predicting biodiesel yield. The optimum conditions obtained through RSM corresponding to maximum biodiesel yield of 93.5± 0.76 %, are found to be: MeOH:seeds ratio (v/w) 7.47, catalyst amount (KOH) 1.7%, reaction time 1788 s, and reaction temperature 317 K.

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