Optimization of mixed base catalyst in the production of Fish oil Biodiesel using Response Surface Methodology (RSM)

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Abstract: The Response Surface Method (RSM) was utilized to obtain the optimal conditions for the fish oil biodiesel via Central Composite Rotatable Design (CCRD). Two process variables viz., homogeneous & heterogeneous catalyst were assessed at five levels, with a total of 13 experiments had been designed and conducted to improve biodiesel yield. A yield of 97.3% fish oil methyl ester (FOME/biodiesel) was obtained at different optimum conditions: 2.20% heterogeneous catalyst & 0.06% homogeneous catalyst concentrations. The observed and predicted values of biodiesel yield were associated in-line.

Keywords: Response Surface Methodology (RSM), Fish oil Biodiesel, Central Composite Rotatable Design (CCRD)

1. Introduction:
Fossil fuel are the source of oil based product, which are getting depleted everywhere throughout the world in a quicker rate. The reason may be increase in demand of petroleum product for augment of industrialization with explosion of population rate [1]. A large portion of the nations on the globe are looking for elective sources of fuel for their energy needs. The outstanding correlation between sustainability, conservation of energy, & great proficiency recommend biodiesel as an alternative fuel [2,3]. Some of the additional benefits which boosts the application of biodiesels are- a renewable source that undergoes complete combustion, non-toxic and less emission of oxides of carbon, oxides of sulphur when compared with conventional diesel [4,5]. The composition of alcohol (methanol/ethanol) and catalyst (basic/acidic) reacts with triglycerides under a transesterification process leads to the formation of biodiesel [6, 7]. The yield of biodiesel is dependent on various reaction parameters of transesterification process viz., catalyst composition, reaction time, methanol: oil ratio, reaction temperature & stirrer speed. Thus, there is a need to optimize these reaction parameters to obtain a better yield of biodiesel & avoid excess usage of resources [8].

In case of optimization synthesis of biodiesel was obtained by varying one parameter at any moment and the response is a function of a single factor, which consumes more time and increases cost of reaction [9]. This system does exclude natural impacts among the factors and it doesn't portray the entire impact of the parameters on the process[10]. However, application of Response Surface
Methodology (RSM) in multivariable system offers a solution to the above problem. It is a research methodology in concentrate the interaction of the parameters utilizing factual strategies. This is useful when large scale manufacturing of the biodiesel is required. Rashid et al. obtained better yield of sunflower oil methyl ester using RSM with the aid of optimized reaction parameters [11]. Yathish et al., experimented RSM to optimize reaction parameters to improve the yield of Scum oil biodiesel (93%) [8]. The authors recommended the use of optimization process by RSM technique, which avoids excessive use of time & resources.

2. Materials & Methods:

2.1 Materials:

The fish oil in dark brown color having less Free Fatty Acid to avoid esterification is purchased from Mangalore, Karnataka. The catalysts viz., sodium hydroxide (homogeneous catalyst) and anhydrous sodium di phosphate (heterogeneous catalyst) and methanol, are purchased from Fisher Scientics, Bangalore, Karnataka.

2.2. Production Method:

The 3 neck flask measuring 500 ml fitted with coiled condenser is placed on a thermostat at a preferred temperature. An average of 650 rpm speed is maintained for magnetic stirrer which is placed inside the flask helping in proper mixing of catalyst and oil. A known mass of fish oil (100g) is added in the 3 neck flask and preheated before the reaction. After sometime a decided amount of sodium hydroxide is added in methanol solution and stirred manually until all the hydroxide compound dissolves. Now the predefined amount of sodium di phosphate is mixed to the solution by stirring. Since sodium di phosphate is a heterogeneous catalyst it doesn’t dissolve in methanol solution. Now this final mixture is poured in the flask containing preheated oil. After the completion of defined time the reaction mixture is poured into a separating funnel and allowed the mixture to cool, which leads to the formation of three separate phases, namely i). Lower phase – catalyst (heterogeneous), ii). Upper phase - fish oil methyl ester and iii). Middle phase – mixture of glycerol and sediments found in the mixture. The catalyst is collected in small beaker for next reaction (5 to 6 trials) whereas the glycerol is removed from the funnel. The methyl ester is allowed for fractional distillation to recollect methanol. Now the fish oil methyl ester is poured into the funnel and washed using water maintained at a pH value of 7 and temperature of 70°C. At every wash some amount of glycerol and soap will be removed, this leads to decreased pH value of methyl ester. After obtaining proper pH value (7) of methyl ester, remove the water content by heating (>100°C).

The yield of ester is expressed as = \( \frac{Ester\ produced\ (g)}{Quantity\ of\ oil\ taken\ for\ reaction\ (g)} \times 100 \)

2.3. Experimental design:

The experimental design is applied in the transesterification reaction for optimizing the variables to yield more methyl esters. The inputs and output of experimental design are homogeneous catalyst, heterogeneous catalyst, reaction temperature, reaction time & methanol: oil ratio and yield of biodiesel respectively. In this research only two inputs are varied and the remaining inputs are kept constant. Optimization is done using RSM based on two independent variables (i.e., homogeneous & heterogeneous catalysts) for five level central composite rotatable designs [13]. This methodology consisting of 13 experiments \((=2^m + 2m +3, m\ stands\ for\ number\ of\ independent\ variables)\) includes 2 replica at the center point which estimates pure error [13]. The independent variables are shown in the Table-1 along with their range and levels.

Referring to few authors the remaining input values viz., Methanol: oil ratio (6:1), reaction temperature (60°C) & reaction time (around 60 min.) were kept constant [14].
In the transesterification response it was watched that the reaction time doesn't influence after it achieves saturation point. In this research the usage of mixed (heterogeneous- major component) catalyst needs more time to react hence the time span is increased [13,14,15].

2.4. Statistical analysis (ANOVA):
Statistical analysis is defined as collecting and scrutinizing data, through which selective samples can be drawn from the total mass [16]. The statistical analysis of the regression equation by ANOVA shows Multiple Correlation Coefficient (R²), which confirms the fitness of the model. Statistical analysis of the data was performed by design package, Design-Expert version 7.0 to evaluate the analysis of variance (ANOVA), sets F value (>95%) & p value (≤5%) for any equation which determines statistical significance of each term. The response of CCRD was fitted with second order polynomial equation. The optimum estimation of the chose factors was gotten by investigating the response surfaces and explaining the regression equation. The empirical regression model equation for a two factor system was taken as

\[ Y = \beta_0 + \beta_1P_1 + \beta_2P_2 + \beta_{11}P_1^2 + \beta_{22}P_2^2 + \beta_{12}P_1P_2 \]  

Where, Y= Predicted response, \(\beta_0\)= Intercept, \(\beta_1\) & \(\beta_2\)= Linear coefficients, \(\beta_{11}\) & \(\beta_{22}\)= Square co efficient, \(\beta_{12}\)= Interaction coefficients, \(P_1\)= Homogeneous catalyst, \(P_2\)= Heterogeneous catalyst.

3. Results & Discussion:
A CCRD was employed in our study to develop a symphysis of the chemical reaction between homogeneous catalyst and heterogeneous catalyst in order to maximize the yield of FOME. Consequently processed and prepared values at different purposes of our study are tabulated in Table-2 & 3. Once the catalyst composition chart is prepared, then the reactions will be carried out to obtain the observed readings. By feeding the observed readings in the software, the predicted readings were obtained in the Table-2. The biodiesel yield was varied from 69.9% to 97.3%. The maximum yield (97.3%) was obtained for 0.6 % (wt/v) of homogeneous catalyst & 2.20 % (wt/v) of heterogeneous catalyst. In all the trials some of the reaction parameters were kept constant viz., molar ratio (6:1), Time (60 Min.) & Temperature (60°C). The utilization of the advanced multiple regression analysis was utilized to get the polynomial condition with the coefficient of full regression model equation and their statistical essentialness was resolved. The equation (ii) of the significant terms obtained from the model in its coded form is as follows:

\[ Y = +96.40 - 1.33P_1 + 4.19P_2 - 6.63P_1P_2 - 0.82P_1^2 - 10.42P_2^2 \]  

Where, Y is the biodiesel yield obtained & \(P_1\) & \(P_2\) are the code forms of homogeneous & heterogeneous catalysts respectively. The positive or negative prefix (+/−) indicates the collaboration and hostile impacts. [17].

The ANOVA showed \(R^2\) value of 0.9979, which confirms the fitness of the model (>0.75 indicates the model is fit). The theoretical values of adj \(R^2\) and the pred \(R^2\) were 0.9963 and 0.9873 respectively, which signifies the model is good. The adequate precision value of the model is 70.517 and the value of C.V % 0.65 confirms the model’s flexibility and reliability [19]. The model F value of 651.57 indicates that the model is significant. Figure 1 shows an acceptable correlation between the predicted and experimental values of biodiesel production. The maximum points (biodiesel yield) are situated in the range of 95–98% and the remaining points are located below 90%. Figure 2 illustrate the interaction between two independent variable [homogeneous catalyst % (wt/v) and heterogeneous catalyst % (wt/v)] on single dependent parameter i.e., biodiesel yield. The biodiesel yield increases significantly by increasing heterogeneous catalyst, whereas the effect of homogeneous catalyst is less. If the value of p stands less than 0.05, then we can confirm about the significance level of \(P_1\) & \(P_2\) [19].
Table-1. Experimental range and values for RSM

| Independent Variables | Range and level |
|-----------------------|----------------|
|                       | -α | -1 | 0 | 1 | α |
| Homogeneous Catalyst, % (wt/v) | 0.06 | 0.20 | 0.55 | 0.90 | 1.04 |
| Heterogeneous Catalyst, % (wt/v) | 1.07 | 1.40 | 2.20 | 3.00 | 3.33 |

Table-2. Experimental process obtained for fish oil

| Standard Order | Homogeneous Catalyst, % (wt/v) | Heterogeneous Catalyst, % (wt/v) | Biodiesel yield (%) | Observed | Predicted | Residual values |
|----------------|--------------------------------|---------------------------------|---------------------|----------|-----------|----------------|
| 1              | 0.20                           | 1.40                            | 75.2                | 75.67    | -0.47     |
| 2              | 0.90                           | 1.40                            | 86.1                | 86.26    | -0.16     |
| 3              | 0.20                           | 3.00                            | 96.6                | 97.31    | -0.71     |
| 4              | 0.90                           | 3.00                            | 81                  | 81.40    | -0.40     |
| 5              | 0.06                           | 2.20                            | 97.3                | 96.64    | 0.66      |
| 6              | 1.04                           | 2.20                            | 93.1                | 92.88    | 0.22      |
| 7              | 0.55                           | 1.07                            | 69.9                | 69.63    | 0.27      |
| 8              | 0.55                           | 3.33                            | 82.1                | 81.49    | 0.61      |
| 9              | 0.55                           | 2.20                            | 96.4                | 96.40    | 0.00      |
| 10             | 0.55                           | 2.20                            | 96.3                | 96.40    | -0.10     |
| 11             | 0.55                           | 2.20                            | 96.2                | 96.40    | -0.20     |
| 12             | 0.55                           | 2.20                            | 96.1                | 96.40    | -0.30     |
| 13             | 0.55                           | 2.20                            | 97                  | 96.40    | 0.60      |

Table-3. ANOVA for response surface quadratic model

| Source            | Sum of Squares | Df | Mean square | F value | p-value prob>F |
|-------------------|----------------|----|-------------|---------|----------------|
| Model             | 1087.64        | 5  | 217.53      | 651.57  | < 0.0001       |
| P1-Homogeneous    | 14.15          | 1  | 14.15       | 42.38   | 0.0003         |
| P2-Heterogeneous  | 140.73         | 1  | 140.73      | 421.53  | < 0.0001       |
| P1P2              | 175.56         | 1  | 175.56      | 525.87  | < 0.0001       |
| P2^2              | 4.66           | 1  | 4.66        | 13.97   | 0.0073         |
| P2^2              | 755.13         | 1  | 755.13      | 2261.86 | < 0.0001       |
| Residual          | 2.34           | 7  | 0.33        |         |                |
| Lack of fit       | 1.84           | 3  | 0.61        | 4.90    | 0.0794         |
| Pure error        | 0.50           | 4  | 0.13        |         |                |
| Cor total         | 1089.98        | 12 |             |         |                |
4. Conclusion:
This research work aim at optimizing the proportions of mixed base catalyst for a better yield of fish oil production. A Response Surface Method used for the optimization process of the proportions of mixed base catalyst keeping the other research parameters as constant. This study revealed that mixed base catalyst with a concentration of 0.06 %(wt/v) of Sodium hydroxide & 2.20%(wt/v) of anhydrous disodium ortho phosphate catalyst compositions gave the optimum yield of 97.3%. The multiple correlation coefficient of RSM viz., $R^2$, adj.$R^2$ & Pred.$R^2$ are 0.9979, 0.9963 & 9873 respectively confirms model is good and fit.

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