"Optimization of Transesterification Reaction Parameters For Fish Oil Biodiesel Production: A Response Surface Methodology Approach"

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Abstract: The Fish oil was used to produce biodiesel by transesterification reaction with methanol as a solvent in presence of a mixture of sodium hydroxide & di-sodium orthophosphate as catalyst concentrations (mixed base catalyst). The optimization of transesterification reaction parameters were done using Response Surface Methodology (RSM) tool. Three process variables were assessed viz., Methanol to Oil Ratio (MOR), Reaction Time (RT) & Reaction Temperature (RTE). To get maximum yield of fish oil biodiesel (FOB), 20 experiments were designed and conducted. A yield of 94.6% FOB was obtained during the transesterification process carried out at the optimized reaction parameters viz., 7.5:1 MOR, 45 minutes RT & 70°C RTE. Statistical analysis of the predicted model by RSM revealed a good agreement between the observed and predicted values. Present research is successful in effectively using RSM tool for optimization of transesterification reaction parameters.

Keywords: Transesterification, RSM, FOB, MOR, RT, RTE

1. Introduction:
Historically, gas and diesel have been utilized as vehicle powers for quite a while. Liquid fuel is available abundantly and considered as a precious resource. But modern man is somehow using this resource unsystematically. Crude oil, the primary source of liquid fuel is found to be expensive to recover as its reserves are depleting [1]. The governments are adapting strategies to develop alternative energy sources to overcome the escalating prices of crude oil. With lot of concerns to the issue of global warming, there are now serious steps been taken to replace crude oil [2]. Thus development & use of alternative fuel which is considered to be less harmful to the environment has received lot of impetus these days. Biofuels are preferred as an alternative fuel to fulfill the requirement for the process of development of society. Biodiesel, one of the classification of biofuel has received lot of attention as it meets the requirements of engine application by exhibiting desired chemical & physical properties [3]. Biodiesels are environmental friendly as it is a clean burning fuel & biodegradable. It is a mono alkyl ester which is being produced from various sources like vegetable oils or animal fat [4, 5].

The parts of fish like head, tail, fins, skin, Viscera etc that are not consumed by human beings are disposed as fish waste. The disposal of fish waste in the large scale causes animal diseases and biological changes by generating high pollution loadings [6,7]. It is also possible to reduce the fish waste by recovering them as marketable by-products. The aquatic waste, which is a source of fat, can be recovered as useful products like fish oil/meal and organic fertilizer. The fish oil obtained by boiling the fish waste can be then converted into a biodiesel through a process called transesterification. Production of biodiesel from animal fat is a technology that exists from quite a long time. Recently, adapting this technology to aquatic resources has evoked public interest. The main reason for this may be due to a significant stress on land-based products to produce biofuels. In the years to come it would be expected that the stress will be even more. Therefore considering energy production from aquatic sources makes sense not only from ecological prospective but from economic point of view too. It is also possible to convert 1 kg of fish waste into 1.13 liters of fish oil biodiesel, using conversion process [8]. Cheng-Yuan Lin et. al, produced FOB from the waste parts of marine fish. This
biodiesel blended with diesel to run the engine has been reported reduction of emission gases and improved engine performance [9]. T.Hari Prasad et. al., concluded from their experimental studies on CI engine powered with blends of FOB that the emission levels of CO, CO₂ & HC is significantly less but increased NOₓ emission. He has also confirmed the higher quality of fish oil biodiesel by comparing some of the properties with commercial diesel in ASTM standards [10]. Through these research works it can be concluded that the fish waste could be used in the production of fish oil biodiesel (FOB). The quality of FOB is good when compared with diesel in terms of emission.

Yathish et. Al., suggested that, if the optimization of transesterification reaction parameters are done the yield of biodiesel could be increased [11]. All attempts in the direction of optimization of variables for a better yield of biodiesel were made by conventional process by carrying out a series of experiments for different variables on a trial and error basis. This results in more number of experiments before arriving at optimized values leading to huge consumption of resources & time. The Statistical method is one which follows some technique called Design of Experimentation (DOE). To overcome this, recently, researchers started exploring the utility of DOE techniques in researches on biodiesel production. The DOE reduce the number of experiments and also provide right proportions of composition, so that with less efforts good results will be obtained. Response Surface Method (RSM), is one of the tool working on DOE technique [12, 13].

RSM is a tool to analyze problems having many independent variables influencing a dependent variable (Response) from a collection of statistical techniques. RSM aims to optimize this response. It is a useful tool for the design and analysis of experiments. It usually works in the following steps: a). Use steepest ascent method to move towards the neighborhood of operating conditions giving optimum response. b). Use special experiment designs to fit a more elaborate model between the response and the factors. c). Use desirability function to optimize more responses at the same time [14].

The present work is distinct as an attempt is made to improve the yield of FOB using reaction parameters viz., MOR, RT & RTE. In the research the optimum values for homogeneous [0.06 % (wt/v)] & heterogeneous [2.2 % (wt/v)] catalysts are considered in order to obtain optimum values of transesterification reaction parameters [13, 15].

2. Design of Experiments (Experimental Design):

The Design of Experimentation (DOE) plays an important role in setting up the transesterification reaction parameters. Response Surface Methodology (RSM) tool is one among DOE, which is used to optimize the transesterification reaction parameters. Design variables considered in the experimentation are methanol to oil ratio (A), reaction time (B, min) and reaction temperature (C, °C), whereas the response variable is biodiesel yield (Y, %) [16]. The effects of these three reaction parameters (variables) are evaluates using five level Central Composite Rotatable Designs (CCRD) viz., -α, -1, 0, +1, +α. The range and the levels of the independent variables considered for the current research are presented in Table-1.

| Table-1: Experimental range and values for RSM |
|-----------------------------------------------|
| Indicators | Independent Variables | Range and level |
|-----------|-----------------------|-----------------|
| A         | Methanol to oil ratio | -α 3.48 -1 4.50 0 6.00 +1 7.50 +α 8.52 |
| B         | Reaction Time (min)   | 34.77 45.00 60.00 75.00 85.23 |
| C         | Reaction Temperature (°C) | 43.18 50.00 60.00 70.00 76.82 |

It is very important to set the number of experiments through statistical analysis, which is calculated using below mentioned equation (1).

\[ N = 2^k + 2k + C \]

Where, k - the number of independent variables and C- replicates at the center point to estimate pure error [12, 15]. In this section the independent variables and the replicas are considered to be 3 and 6 respectively.
The independent variable are identified as MOR, RT & RTE respectively. The replicas confirms the correctness of response values and the methods used. Now substitute the values to obtain the number of experiments using the above equation. The number of experiments to be conducted are,
\[ N = 2^2 + 2k + C = 2^3 + 2 \times 3 + 6 = 20 \]

For all the 20 experiments the reaction parameters viz., MOR, RT & RTE proposed by the software (RSM tool) is given in Table-2. For each experiment the obtained yield of FOB is tabulated (in Table-2) below as observed values. During the conduction of each experiment the optimum concentration of homogeneous and heterogeneous catalysts are set to 0.06 % (wt/v) & 2.20 % (wt/v) respectively.

2.1. Method:
The conversion of oil to biodiesel was done through transesterification process. The Experimental set up consisting of 3-neck flask for transesterification reaction, stirrer for proper mixing of solution, a thermostat for temperature maintenance and condenser to avoid the evaporation of solution contents. A known mass of oil is poured into 3-neck flask and is preheated (temperature more than atmospheric) before the start of transesterification reaction, which helps in smooth initiation of reaction. A definite mixture of homogeneous catalyst (NaOH) & heterogeneous catalyst (Na2HPO4) were added to the predefined MOR and the mixture was poured into the preheated oil. The fish oil solution was heated (>60°C) to preferred time (60 min) for complete transesterification reaction. Once the transesterification process completes, pour the solution in funnel for cooling and separation process. After some time the funnel prepares three layers viz., top layer mixture of slight methanol and ester, middle layer glycerol and bottom layer contains remained catalyst (which should be collected for next reaction). Separate bottom two layers by filtration process and retain the remaining ester for distillation process. The distilled and heated water is used to remove the basic content in the ester till the pH of solution reaches 7. Now the ester is heated above the boiling point of water to obtain pure ester and then allow it for cooling. The ester/methyl ester is called biodiesel/fish oil biodiesel (FOB). The yield of methyl ester is calculated from the equation (2) & tabulated as observed value (in 4th column of Table-2).

\[
\text{Yield} = \frac{\text{Mass of FOB produced (g) \times 100}}{\text{Mass of fish oil taken for reaction (g)}}
\]

Yield (Example) = \( \frac{243.3 \times 100}{250} = 97.3 \% \)

To validate the experimental results the RSM tool also predicted the Response value (yield of FOB). Further statistical analysis was carried out through ANOVA to check the significance of the group of experiments (Model). This helps in finding the optimum values of MOR, RT & RTE.

3. Result and Discussion:
3.1. Optimization of FOB Production by RSM:
A CCRD was employed in our study to find the optimum relations between the transesterification reaction parameters in order to maximize the biodiesel production. The predicted values obtained through the statistical analysis are tabulated in Table-2. In the Table-2 the biodiesel yields obtained are ranging from 70.1% to 94.6%. The minimum biodiesel yield was 70.1% which is obtained at 3.48:1 MOR, 60 min RT and 60 °C RTE. A maximum biodiesel yield of 94.6% was obtained at 7.5:1 MOR, 45 min RT and 70 °C RTE.

Table 2: Yield of FOB for different combinations of reaction parameters

| Standard Order | MOR  | RT (min) | RTE (°C) | Biodiesel yield (%) |
|---------------|------|----------|----------|---------------------|
|               |      |          |          | Observed Values     | Predicted Values | Residual Values |
| 1             | 4.50 | 45.00    | 50.00    | 73.2                | 73.02            | 0.18            |
| 2             | 7.50 | 45.00    | 50.00    | 83                  | 82.61            | 0.39            |
| 3             | 4.50 | 75.00    | 50.00    | 78.1                | 77.99            | 0.11            |
| 4             | 7.50 | 75.00    | 50.00    | 85.2                | 85.33            | -0.13           |
A polynomial equation of the developed regression model and its statistical significance was obtained by Multiple Regression Analysis (MLA). The obtained equation in its coded form is as follows:

\[ Y = +85.16 + 5.67 A + 0.98 B + 3.55 C - 0.56 A^2 + 1.44 A\times B - 0.94 B\times C - 1.88 A^2 + 1.78 B^2 - 1.76 C^2 \]  

Where, Y, A, B & C are the coded forms of biodiesel yield (response value), MOR, RT (min) and RTE (°C) respectively.

Table-3: ANOVA for a developed model

| Source     | Sum of Squares | Df | Mean square | F value | p-value prob>F | Significance/ Non-Significance |
|------------|----------------|----|-------------|---------|----------------|-----------------------------|
| Model      | 802.49         | 9  | 89.17       | 753.43  | < 0.0001       | Significant                 |
| A-MOR      | 438.92         | 1  | 438.92      | 3708.73 | < 0.0001       |                             |
| B-RT       | 13.20          | 1  | 13.20       | 111.55  | < 0.0001       |                             |
| C-RTE      | 172.11         | 1  | 172.11      | 1454.27 | < 0.0001       |                             |
| A * B      | 2.53           | 1  | 2.53        | 21.39   | 0.0009         |                             |
| A * C      | 16.53          | 1  | 16.53       | 139.69  | < 0.0001       |                             |
| B * C      | 7.03           | 1  | 7.03        | 59.41   | < 0.0001       |                             |
| A^2        | 51.16          | 1  | 51.16       | 432.29  | < 0.0001       |                             |
| B^2        | 45.41          | 1  | 45.41       | 383.71  | < 0.0001       |                             |
| C^2        | 44.66          | 1  | 44.66       | 377.37  | < 0.0001       |                             |
| Residual   | 1.18           | 10 | 0.12        |         |                |                             |
| Lack of Fit| 0.83           | 5  | 0.17        | 2.35    | 0.1851         | Non-Significant             |
| Pure Error | 0.35           | 5  | 0.071       |         |                |                             |
| Cor Total  | 803.67         | 19 |             |         |                |                             |

R^2: 0.9985 ; Pred R^2: 0.9913; Adj R^2: 0.9972 Adequate Precision: 99.350 ; C.V %: 0.41

Table-3 gives results of ANOVA of RSM model for transesterification reaction parameters. The fitness of the model can be confirmed through the R^2 value (>0.75 indicates model is fit), which is 0.9985. The total variation of the data evaluated by this model can able to explain 99.85% of total variation for experimental parameters with their mutual interactions. The theoretical values of adj R^2 and the pred R^2 were 0.9972 and 0.9913 respectively. Since these values are close to 1 it indicates that the model is fit & good. The statistical analysis carried out is indicating that the developed regression model is significant with a F value of 753.43 and a p-value <0.0001 as given in Table 3. The p-value will be <0.5 only if the interaction between reaction variables are too good[13]. Since the p-value is far less than 0.5 a good interaction between the reaction variables
is confirmed in the developed model. In this analysis all the source values were significant. In Fig.1 the actual & predicted values show a good correlation. Fig.2. are the 3 dimensional Surface plots representing graphically the interaction between the reaction parameters and their effect on the yield. The biodiesel yields were analyzed through the interaction between any two of reaction parameters out of three. Each cases were observed and named as AB, AC & BC respectively. The plots drawn below shows the variation of MOR, RT & RTE linked to biodiesel, but the catalyst composition (homogeneous catalyst 0.06% (wt/v) & heterogeneous catalyst 2.2% (wt/v)) remains the same in entire set of experiments.

Plot-AB represents the significant interaction between RT and MOR. The plot indicates that the increase in the yield with the increase in MOR is significant. However, RT has little effect on the yield. Plot-AC shows the interaction between RTE and MOR on the biodiesel yield. Here we observe that as both the values of RTE & MOR increases then the biodiesel yield also increases significantly. The maximum yield is seen when the MOR is at 7.5:1 & 45 min of RT. Plot-BC shows the interaction between RTE and RT parameters on the biodiesel yield. It indicates a considerable increase in the yield of biodiesel as RTE increases. It is observed that the RT doesn’t affect more in increasing yield of biodiesel. From the above discussion it can be concluded that out the three transesterification reaction parameters, MOR and RTE significantly has an effect on the biodiesel yield compared to RT.

![Fig.1: Actual yield vs. predicted yield](image1)

![Fig.2: Surface plots (AB, AC, BC) of conversion to biodiesel (%)](image2)

![Fig.3: Numerical optimization parameters for biodiesel yield](image3)

**3.2. Process optimization:**

To validate the process of optimization it is important to check for desirability function. The desirability function of RSM tool gives the yield as 94.46% when the values of A,B & C are 7.5:1, 45 min & 70°C respectively as indicated in Fig.3. The value of desirability for the above mentioned conditions is 0.994. But the optimized yield obtained by experimentation is found to be 94.6% for the same values of transesterification reaction parameters. The difference between the optimized yields obtained by RSM tool & by experimental method is 1.4%, which is relatively small. This small error has brought down the value of desirability from 1 to 0.994. Hence from this analysis of desirability function it can be concluded that the
transesterification reaction parameter viz., 7.5:1 of MOR, 45 min of RT & 70°C of RTE are the optimized values to obtain a better yield of FOB.

4. Conclusions:

This research was aimed at understanding the optimized transesterification parameters for obtaining a higher yield of fish oil biodiesel by RSM approach. The results of investigation has discovered that RSM is an effective tool to optimize the transesterification reaction parameters for a better yield. The statistical analysis confirms the significance of the model predicted by RSM. The tool is found to be effective in validating the experimental results of yield obtained at optimized reaction parameters.

The study also reveals that the transesterification reaction parameters viz., MOR of 7.5:1, RT of 45 min & RTE of 70°C can be considered to be optimal to obtain a higher yield of 94.6% when a mixed base catalyst is used for the production of FOB. The desirability function confirms the process optimization with an error of 1.4 % with a desirability value of 0.994.

The present research will open up avenues for researchers to further investigate on the optimization of other variables to obtain higher yield of biodiesel production and to the entrepreneurs venturing into the idea of converting fish waste into a more useful fish oil biodiesel.

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