Optimization of Reducing Ffa Content of Waste Cooking Oil by Using Response Surface Methodology

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Abstract

Waste cooking oil has high free fatty acid (FFA). It impact to low yield of biodiesel production. Thus, reducing FFA is one of important process as feedstock of biodiesel. This study aims to investigate the optimum condition of three important process variables which are acid concentration, molar ratio of methanol and oil, and irradiation time with the 45°C of irradiation temperature for reducing FFA. The synthesis is assisted by ultrasonic irradiation. It conducted by acid esterification with H$_2$SO$_4$ and methanol. Optimization is conducted by Response Surface Methodology (RSM) with central composite design (CCD). The optimum condition of response for reducing FFA less than 1% were found to be 7.22:1 of methanol to oil molar ratio, 0.92% wt of H$_2$SO$_4$, and 26.04 minutes of irradiation time. It has been observed that ultrasonic system reduces FFA content significantly compared to conventional method.

Introduction

Biodiesel production is more attractive as fuel due to its feedstock availability and environmental issue. Biodiesel is considered to decrease the dependence to fossil fuel. Waste cooking oil is potential feedstock to be developed since it is non-edible oil and large availability. Thus, it has potential for mass production [1]. However, it has problems to be biodiesel feedstock due to its free fatty acid content. It is reduced by acid esterification. Esterification is the reaction of two immiscible phases. The less dense phase dissolves the catalyst in the alcohol, while the other phase contains oil. The reaction between the two immiscible phases occurs in the area of the interface between the liquids. Interface area between phases should be increased by vigorous mixing [2]. As we all know, ultrasonic radiation is a means of emulsifying immiscible liquids.

This study is conducted by ultrasonic irradiation. It produces bubble cavitation around boundary phase between the alcohol phase and the oil. Emulsification is generated during rupture of cavitation bubbles that break boundary phase. Ultrasound impacts one liquid on another liquid [3]. Temperatur will increase locally at boundary phase due to cavitation, thereby transesterification reaction enhances significantly[4–5].

Response surface method (RSM) is a powerfull statistical method that has been carried out in many studies [6]. Multiple regression and correlation analysis are used as tools to evaluate the influence of two or more independent factors toward dependent variables. In addition, the central composite design (CCD) has been optimized in some chemical processes and biomass technology. The main advantage is to reduce required experimental numbers to provide enough information to obtain acceptable findings statistically. It has been successfully carried out to optimize the production of biodiesel in oil feedstocks, including Madhuca indica, Jatropha curcas oil, and animal fats [7–10].

In the recent study, esterification based acid is used to reduce high free fatty acid (FFA) of waste cooking oil. Optimization of process variable to be less than 1% using RSM for design of experiments.
Materials And Methods

Materials

Waste cooking oil was purchased from fried chicken restaurant in Padang, West Sumatera, Indonesia. Methanol and H_2SO_4 were supplied from Systerm. Its characteristics are reported in Table 1.

| Characteristics                          | Value   |
|-----------------------------------------|---------|
| % FFA                                   | 14.2    |
| Acid Value, mg KOH/g oil                | 28.258  |
| Moisture content, % w/w                 | 2.31    |
| Iodine Value, mg/g oil                  | 102.85  |
| Saponification Value, mg KOH/g oil      | 192.52  |
| Viscosity, cSt                          | 46.85   |
| Density at 20°C, g/cm³                  | 0.9114  |

Methods

Acid Esterification Process

Acid esterification was carried out using equipment setup as shown in Fig. 1. The ultrasonic processor used Trans-O-Sonic from Shanti Industrial Estate, India with frequency 30 ± 3 KHz and power of 250 Watt. Approximately 12 g of oil was poured in the round bottom flask. It was heated 45°C and irradiated by ultrasonic. Subsequently, the certain amounts of methanol and sulfuric acid were poured to the oil. Temperature was kept constant during esterification process. Heating and ultrasonic irradiation were stopped after irradiation has reached the irradiation time. The flask was immersed in cold water immediately for stopping the irradiation. The mixture was stand until separate two layers. The bottom layer was drained whereas the upper layer was washed by hot water for removing the impurities then dried for further analysis (% FFA).

Experimental Design

This study employed RSM with Central Composite Design (CCD). Three process variables are set as independent variables. Those are concentration of sulfuric acid (% H_2SO_4) (C), molar ratio of methanol to oil (M), and irradiation time (t). Dependent variable is free fatty acid (%FFA). A five-level-three-factors CCD
was carried out in this study during 20 experiments \((2^k + 2k + 6)\). \(k\) is the number of independent variables. The level of uncoded and coded (actual) of independent variables are described in Table 2.

### Table 2

Independent variable and levels used for CCD in acid transesterification process

| Variable                                | Symbol | Level\(^a\) |
|-----------------------------------------|--------|-------------|
| Methanol to oil molar ratio             | M      | 2.30 : 1    |
|                                         |        | 4 : 1       |
|                                         |        | 6.50 : 1    |
|                                         |        | 9 : 1       |
|                                         |        | 10.70 : 1   |
| \% \(\text{H}_2\text{SO}_4\) (%w)      | C      | 0.16        |
|                                         |        | 0.5         |
|                                         |        | 1.0         |
|                                         |        | 1.5         |
|                                         |        | 1.84        |
| Irradiation Time (minute)               | t      | 3.20        |
|                                         |        | 10          |
|                                         |        | 20          |
|                                         |        | 30          |
|                                         |        | 36.80       |

\(^a\)Transformation of variable levels from coded (X) to uncoded could be obtained as:

\[ M_u = 6.50 + 2.50X, \ C_u = 1 + 0.5X, \ t_u = 20 + 10X \]

Replication were conducted twice for all experimental runs. The value of alpha \((\alpha)\) was fixed 1.68. The central point (zero level) for each independent variable was 6.50 : 1 for molar ratio of methanol and oil, 1\% \(\text{H}_2\text{SO}_4\) of \% catalyst, and 20 minutes for irradiation time. Experiments are conducted in random order.

### Determination of Free Fatty Acid content (% FFA)

FFA content was examined as percentage of oleic acid. Potassium hydroxide (KOH) was used as standard alkali solution. This quantitative analysis was examined based on AOAC (Association of Official Agricultural Chemists) Official Method Cd 3a-63.

### Analysis Statistically

Second-order polynomial was applied in analysis as shown in Eq. 1:

\[
y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i>j}^{3} \beta_{ij} x_i x_j + e \quad \text{Equation 1}
\]

Where \(y\) is the response (percentage of free fatty acid, % FFA); \(\beta_0\) is intercept, \(\beta_i\) is linear constant coefficients, \(\beta_{ii}\) is quadratic constant coefficients, and \(\beta_{ij}\) is interaction constant coefficients. \(x_i\) and \(x_j\) are the uncoded independent variables; \(e\) is the error. Design Expert 6.0.10 (STAT-EASE Inc) is applied to examine analysis of regression and analysis of variance (ANOVA). Validation of equation is conducted by confirmatory experiments using combinations of independent variables. It is within the experimental area but not part of the original experimental design \([7]\). The coefficient of determination \((R^2)\) is used to evaluate the quality of the model fit, and the response surface graph is drawn using the fitted quadratic polynomial equation obtained through regression analysis.
Results And Discussion

Model Fitting and ANOVA

Table 3 shows the experimental and predicted values of the free fatty acid response percentage obtained at the design point. All variables are displayed in coded and non-coded form.

| No. | M  | C   | t   | %FFA |
|-----|----|-----|-----|------|
|     | coded | Actual | coded | actual | coded | actual | Experimental | Predicted |
| 1   | -1  | 4:1  | -1  | 0.5  | -1   | 10     | 6.21       | 6.12      |
| 2   | 1   | 9:1  | -1  | 0.5  | -1   | 10     | 2.02       | 2.20      |
| 3   | -1  | 4:1  | 1   | 1.5  | -1   | 10     | 4.45       | 4.70      |
| 4   | 1   | 9:1  | 1   | 1.5  | -1   | 10     | 4.01       | 3.98      |
| 5   | -1  | 4:1  | -1  | 0.5  | 1    | 30     | 3.32       | 3.32      |
| 6   | 1   | 9:1  | -1  | 0.5  | 1    | 30     | 0.41       | 0.12      |
| 7   | -1  | 4:1  | 1   | 1.5  | 1    | 30     | 1.31       | 1/10      |
| 8   | 1   | 9:1  | 1   | 1.5  | 1    | 30     | 1.05       | 1.10      |
| 9   | -1.68 | 2.3:1 | 0   | 1.0  | 0    | 20     | 4.21       | 4.23      |
| 10  | +1.68 | 10.7:1 | 0   | 1.0  | 0    | 20     | 0.89       | 0.94      |
| 11  | 0   | 6.5:1 | -1.68 | 0.16 | 0    | 20     | 2.10       | 2.21      |
| 12  | 0   | 6.5:1 | +1.68 | 1.84 | 0    | 20     | 1.88       | 1.84      |
| 13  | 0   | 6.5:1 | 0   | 1.0  | -1.68 | 3.20  | 6.20       | 5.99      |
| 14  | 0   | 6.5:1 | 0   | 1.0  | +1.68 | 36.80 | 0.94       | 1.22      |
| 15  | 0   | 6.5:1 | 0   | 1.0  | 0    | 20     | 0.97       | 1.26      |
| 16  | 0   | 6.5:1 | 0   | 1.0  | 0    | 20     | 1.23       | 1.26      |
| 17  | 0   | 6.5:1 | 0   | 1.0  | 0    | 20     | 1.42       | 1.26      |
| 18  | 0   | 6.5:1 | 0   | 1.0  | 0    | 20     | 1.23       | 1.26      |
| 19  | 0   | 6.5:1 | 0   | 1.0  | 0    | 20     | 1.32       | 1.26      |
| 20  | 0   | 6.5:1 | 0   | 1.0  | 0    | 20     | 1.41       | 1.26      |

Quadratic polynomial model of FFA are predicted by applying least square technique and the multiple regression coefficients of linear and quadratic terms of M, C and T shown in Table 4.
Table 4 Regression coefficients of predicted quadratic polynomial model for acid catalyzed esterification

| Term          | Regression coefficients |
|---------------|-------------------------|
| Intercept     | 1.26                    |
| $\beta_0$     |                         |
| Linear        |                         |
| $\beta_1$     | -0.98                   |
| $\beta_2$     | -0.11                   |
| $\beta_3$     | -1.42                   |
| Quadratic     |                         |
| $\beta_{11}$  | 0.47                    |
| $\beta_{22}$  | 0.27                    |
| $\beta_{33}$  | 0.83                    |
| Interaction   |                         |
| $\beta_{12}$  | 0.80                    |
| $\beta_{13}$  | 0.18                    |
| $\beta_{23}$  | -0.20                   |

Data generates a quadratic polynomial equation. Predicted value of % free fatty acid as shown below (in terms of the code factors):

$$y = 1.26 - 0.98M - 0.11C - 1.42t + 0.47M^2 + 0.27C^2 + 0.83t^2 + 0.80MC + 0.18 Mt - 0.20Ct......Equation 1$$

Where y is the response of %FFA, while M is actual values of methanol to oil molar ratio, C is % $H_2SO_4$ as catalyst and t is irradiation time. Analysis of the model statistically was carried out to examine adequacy of the empirical model and ANOVA. Results are summarized in Table 5.

Table 5 Analysis of variance (ANOVA) for response surface quadratic model
### Table

| Source         | Sum of squares | Degrees of freedom | Mean squares | F-value | P-value |
|----------------|----------------|--------------------|--------------|---------|---------|
| Model          | 59.04          | 9                  | 6.56         | 128.75  | <0.0001 |
| Residual       | 0.51           | 10                 | 0.051        |         |         |
| Lack of fit    | 0.37           | 5                  | 0.074        | 2.70    | 0.1494  |
| Pure error     | 0.14           | 5                  | 0.028        |         |         |
| Cor total      | 59.55          | 19                 |              |         |         |

$CV = 0.97, \quad R^2 = 0.9914, \quad Adj.R^2 = 0.9837, \quad Predicted R^2 = 0.9452, \quad Adeq Precision = 37.653$

The model F value of 128.75 indicates that the model is valid, and the p value of the model is less than 0.0001, which indicates that the model term is very important in predicting the response value and inferring the applicability of the model. The lack of fit is the weighted sum of the squared deviations between the average response of each parameter level and the corresponding fit. The p-value for lack of fit is 0.1494, indicating that it is not significant relative to pure error. The inconspicuous fit is not good. The fitted F value is 2.70, which means that when the model is fitted to the observed experimental data, the possibility of such a large underfitting due to noise is 14.94%. CV of the model is 0.97 that closer to unity. It indicated reliability of fitted model is high. The quality of the modelfit was examined by the coefficient of determination ($R^2$). The $R^2$ value is between 0 and 1. More closer to 1 indicated reliable model.

The study obtained $R^2 0.9914$. It shows that 99.14% of the experimental data is compatible with model. The adjusted determination coefficient (adjusted R2) value is 0.9837, which is close to R2. It shows the experimental has strong correlation to predicted values and explains any changes in the response. Normality plot of data between student residuals and residual are shown in Fig. 2.

It shows that there is a characteristic dispersion of constant variables in the data. The model adequately explains the experimental range studied.

### Interaction of Parameters to % FFA

Figure 3a shows the effect of %H$_2$SO$_4$ and molar ratio of methanol and oil at 20 minutes of irradiation time and 45°C of temperature. Percentage of H$_2$SO$_4$ has more significant effect to reducing FFA compared to methanol and oil ratio. Interaction between %H$_2$SO$_4$ and molar ratio of methanol and oil has positive effect and significant to the reducing FFA content. FFA content decreased with increasing of %H$_2$SO$_4$ and molar ratio of methanol and oil. However, for achieving FFA content less than 1%, employing H$_2$SO$_4$ is less than 1.18% and molar ratio of methanol is more than 7.23:1.
Figure 3b represents the effect of irradiation time at 1%H₂SO₄ and molar ratio of methanol and oil at 45°C of temperature. Irradiation time has more significant effect to reducing FFA compared to molar ratio of methanol and oil. According to plot, FFA content decreased with the increasing molar ratio of methanol and oil. Whereas Fig. 3c represents the effect of %H₂SO₄ and irradiation time. In interaction between %H₂SO₄ and irradiation time, irradiation time has more significant effect to the reducing the FFA content compared to %H₂SO₄.

Process Optimization

Software design expert 6.0.10 is applied to examine process optimization by solving the regression equation (Eq. 1). The model is used to examine the process variable with the smallest FFA content. The optimized result at 45°C is that molar ratio of methanol and oil is 7.22:1, 0.92 wt% H₂SO₄ and 26.04 minutes of irradiation time. The model predicts that the lowest FFA content obtainable under these optimal conditions is 0.5%.

Verification of Predictive Model

Optimum response value was tested to verify model predicted value. It has been examined to be the optimum response through the RSM optimization method, and is also used to verify the experiment and use the model equation to predict the response value. Table 6 shows the predicted and experimental response values under the best conditions.

| Methanol to oil molar ratio (%w/w) | % H₂SO₄ (%w/w) | Irradiation time (min) | Reaction temperature (°C) | % FFA experimental | % FFA predicted |
|-----------------------------------|-------------|----------------------|--------------------------|--------------------|-----------------|
| 7.22                              | 0.92        | 26.04                | 45                       | 0.61               | 0.50            |

The experimental value of the FFA content is 0.61%. The experimental value is closer to the predicted value of the model. The results show the effectiveness of the RSM model, which is sufficient to reduce FFA content for esterification.

Comparison between Ultrasonic Irradiation and Conventional Method

A comparison of the effect of ultrasonic irradiation in reducing FFA content was conducted. Results were presented in Fig. 4.

Figure 4 shows that catalyst performance was more effective with ultrasonic irradiation compared to conventional method. Employing equal amount of methanol and oil (6.50:1) in achieving 1% FFA, acid esterification with ultrasonic irradiation need 0.63% H₂SO₄ and 27.54 minutes, whereas by conventional method need 0.81% H₂SO₄ and 108.40 minutes. It indicates that ultrasonic irradiation reduce catalyst
utilization around 21.69% and 74.59% of reaction time. Ultrasonic irradiation reduced reaction time because ultrasonic generated cavitation and increased mass transfer. Ultrasonic cavitation provided the necessary activation energy in acid esterification. Employing equal %H₂SO₄ around 1%, by ultrasonic irradiation need 5.61:1 molar ratio of methanol and oil whereas by conventional method need 5.82:1. It indicated that ultrasonic reduced methanol to oil molar ratio around 3.61%.

**Conclusion**

In summary, the Response Surface Methodology (RSM) with central composite design (CCD) is successfully conducted to the model to optimize the independent variables for acid esterification using ultrasonic irradiation. Ultrasonic irradiation is an effective method to reduce FFA content and save time. The effect of irradiation time was more significant compared to % H₂SO₄ and molar ratio of methanol and oil whereas %H₂SO₄ was more significant compared to methanol to oil molar ratio in reducing FFA content by acid esterification process. RSM generated reliable model in predicting the FFA content precisely. Further, it generated the optimum value for independent parameter. Those were molar ratio of methanol and oil of 7.22:1, H₂SO₄ concentration of 0.92%, and 26.04 minutes of irradiation time. Under these conditions, the FFA content can be obtained less than 1%.

**Abbreviations**

FFA Free Fatty Acid

RSM Response Surface Methodology

CCD Central Composite Design

C concentration of sulfuric acid

M molar ratio of methanol to oil

t irradiation time

k number of independent variables

AOAC Association of Official Agricultural Chemists

KOH Potassium hydroxide

**Declarations**

**Ethics approval and consent to participate**

Not applicable
Consent for publication
Not applicable

Availability of data and materials
Presented in the main paper

Competing interests
The authors declare that we have no competing interests

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Authors' contributions
Sri Rizki Putri Primandari contributes in conducting all experiments and writing the manuscript.

Andril Arafat contributes in analysis and interpreting data by using software

Arwizet contributes in preparing material and setting equipment. He also contributes in proof reading the manuscript.

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