PROCESS OPTIMIZATION OF CRUDE PALM OIL BIODIESEL PRODUCTION BY RESPONSE SURFACE METHODOLOGY

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ABSTRACT

The main propose of this research is to develop a two-step biodiesel production technique from crude palm oil. Response surface methodology (RSM) was applied for the determination of optimum condition on both esterification and transesterification steps. Crude palm oil biodiesel obtained from RSM met the ASTM biodiesel standard in term of methyl ester content.

Keywords: Crude palm oil, Biodiesel, Esterification, Transesterification

INTRODUCTION

Biodiesel is increased attention as an alternative, non-toxic, biodegradable, and renewable diesel fuel. Biodiesel is usually produced by the transesterification of vegetable oil or animal fat with short chain alcohol such as methanol or ethanol (Guruet al., 2009). Biodiesel has higher oxygen content than petroleum diesel and its use in diesel engines have shown great reductions in emission of particulate matter, carbonmonoxide, sulfur, polyaromatics, hydrocarbons, smoke and noise. In addition, burning of vegetable-oil based fuel does not contribute to net atmospheric CO₂ levels because such fuel is made from agricultural materials which are produced via photosynthetic carbon fixation (Alptekin et al., 2010).

Esterification reaction is a preferred pretreatment process for CPO with an alcohol which converts FFA to methyl ester and commonly uses a strongly acidic liquid catalyst, such as sulfuric acid. The reaction is show in Equation (1)(Canakci et al., 2001).

\[
\text{RCOOH + CH}_3\text{OH} \xrightleftharpoons{\text{H}^+} \text{RCOOCH}_3 + \text{H}_2\text{O}
\]

Fatty acid Methanol Methyl ester Water (1)

Transesterification reaction is the reaction of raw material (Triglyceride) with an alcohol to form methyl ester and glycerol. Alcohols such as methanol and ethanol are the most frequently employed. This
research, methanol is used as an appropriate alcohol and potassium hydroxide catalyst. The reaction is show in Equation (2).

\[
\begin{align*}
\text{Triglyceride} & \quad \text{Methanol} & \quad \text{Methyl ester} & \quad \text{Glycerol} \\
\end{align*}
\]

Response surface methodology (RSM) is a useful statistical technique which has been applied in research into complex variation process. The multiple regression and correlation analyses are used as tools to assess the effects of two or more independent factors on the dependent variable. Furthermore, the central composite design (CCD) of RSM has been applied in the optimization of several biotechnological and chemical processes (Jeong et al., 2009). Its main advantage is the reduced number of experimental runs required to generate sufficient information for a statistically acceptable results. RSM has been successfully applied for optimization of biodiesel production in fat and oil feed stock (Ghadge et al., 2006).

In this work, a two-step catalyzed process is used for the production of biodiesel from CPO. Sulfuric acid is selected as an acid catalyst at the first step to reduce the amount of FFA. As for the second step, potassium hydroxide is then used to catalyze the transesterification reaction in which triglyceride reacted with methanol. The optimized through response surface methodology (RSM) is applied for both steps. Special attention is paid to optimize the first step being the acid catalyzed (esterification) and process variables such as methanol to oil molar ratio, sulfuric acid concentration and reaction time. In the second step being the alkali catalyzed process (transesterification) and process variables such as methanol to oil molar ratio, KOH concentration and reaction time.

EXPERIMENTAL

Materials

Crude palm oil (CPO) used in the research was obtained from Phatum vegetable oil Co, Ltd, (Thailand). This oil had an initial FFA content of 6.58 %wt. Chemicals were of analytical grade included 98 % sulfuric acid and 98 % methanol.

Esterification step

The esterification step was carried out with 10 g of CPO and the calculated amounts of sulfuric acid and methanol (ratio of methanol to oil) were then mixed to oil in 50 ml of three necked flask equipped with reflux condenser and stirrer. That all components was heated up to the desired temperature using paraffin oil bath and a magnetic hot plate stirrer with temperature controller at 60 °C. The speed of the stirrer was kept constant at 600 rpm throughout the experiment. The optimization useful RSM statistical technique had been applied in experiment into complex variation process. At the end of the reaction, the water-soluble components were separated from the product in a separation funnel for 60 min. The esterifield oil product was washed by hot water several times until the washing became clear. Then the washed methyl ester was dried at 120 °C, and the FFA content in the esterified oil was determined by titration with sodium hydroxide.
Transesterification step

The transesterification step was performed on the product from the esterification process by using esterified oil 10 g and the calculated amounts of potassium hydroxide and methanol (ratio of methanol to oil) were then mixed to esterified oil in 50 ml of three necked flask equipped with reflux condenser and stirrer. That all components was heated up to the desired temperature using paraffin oil bath and a magnetic hot plate stirrer with temperature controller at 60 °C. The speed of the stirrer was kept constant at 600 rpm throughout the experiment. The optimization useful RSM statistical technique had been applied in experiment into complex variation process. At the end of the reaction, the methyl ester component was separated in a separation funnel until to phase separation. This resulted in the formation of an upper phase consisting of methyl ester and a lower phase containing glycerol. After separation of the layers by gravity separation, the methyl ester was purified by washing with hot water several times until the washing became clear. The washed methyl ester was dried at 120 °C for 60 min, and the purified methyl ester was analyzed amount of fatty acid methyl ester (FAME) by gas chromatography (GC) in afterwards.

Experimental design

A 5-level-3-factor central composite design (CCD) was employed in esterification step optimization requiring 20 experiments. Methanol to oil molar ratio (M), sulfuric concentration (C) and reaction time (T) were the independent variables to optimize the free fatty acid (FFA) content of CPO. As for transesterification study, requiring 20 experiment. Methanol to oil molar ratio (M), potassium hydroxide concentration (C) and reaction time (T) were the independent variables to optimize the percentage of fatty acid methyl ester (FAME). The code and uncoded levels of the independent variables were show in table 1 and 2 respectively.

The experimental data obtained by following the above procedures were fit to second order polynomial equation as show in Equation (3).

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

(3)

Where y is the response (%FFA or %FAME); \(x_i\) and \(x_j\) are uncoded independent variables and \(\beta_0\), \(\beta_i\), \(\beta_{ii}\) and \(\beta_{ij}\) are intercept, linear, quadratic and interaction constant coefficients, respectively. SPSS package was used for regression analysis of variance (ANOVA) and response surface methodology was performed using the SPSS software. Response surface plots was developed using the fitted quadratic polynomial equation obtain from regression analysis, holding one of the independent variables at constant value corresponding to the stationary point and changing the other two variables. Confirmation experiments were carried out to validate the equation, using combination of independent variable which were not part of the original experimental design but which the experimental region (Bhatti et al., 2008)

| Table 1. Independent variables and levels used for CCD for the esterification step. |
|---------------------------------|-----------------|-----------------|---|---|---|
| Independent variable            | Symbols (uncoded) | Code levels     | -1.68(-α) | -1 | 0  | +1 | +1.68(+α) |
| Methanol to oil molar ratio     | M               | 0.66            | 1           | 1.5 | 2  | 2.34       |
| H₂SO₄ concentration % (wt)      | C               | 0.16            | 0.5         | 1   | 1.5 | 1.84       |
| Reaction time (min)             | T               | 39.6            | 60          | 90  | 120 | 140.4      |
Table 2. Independent variables and levels used for CCD for the transesterification step.

<table>
<thead>
<tr>
<th>Independent variable</th>
<th>Symbols (uncoded)</th>
<th>Code levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol to oil molar ratio</td>
<td>M</td>
<td>0.96 3 6 9 11.04</td>
</tr>
<tr>
<td>KOH concentration %(wt)</td>
<td>C</td>
<td>0.16 0.5 1 1.5 1.84</td>
</tr>
<tr>
<td>Reaction time (min)</td>
<td>T</td>
<td>39.6 60 90 120 140.4</td>
</tr>
</tbody>
</table>

Free fatty acid (FFA) content

The FFA content was determined via AOCS official method ca 5a-40. 7 g of sample was introduced into 200 ml flask, after which 75 ml of ethanol and 2 ml of 1% phenolphthalein were added to the reactant. The mixed solution was titrated with 0.1 N sodium hydroxide standard solution. The FFA content was calculated in accordance with the following Equation (4)

\[
\%FFA = \frac{(A-B) \times N \times 28.2}{W}
\]

In which A is milliliter of sodium hydroxide solution titrated with sample, B is milliliter of sodium hydroxide solution titrated with blank, N is the concentration of solution hydroxide in normality unit and W is the weight in gram of sample.

Fatty acid methyl ester content (FAME)

The FAME was measured via standard EN 14103. The analyses were conducted on a gas chromatography (Agilent Technologies GC-68901) using a Based silica capillary column (AB-WAX, Agilent technologies, USA) and a flame-ionization detector with an injection temperature of 270 °C, and a detector temperature of 270 °C. The spilt ratio was 30:1. The FAME content was calculation via the following Equation (5)

\[
\%FAME = \frac{(\Sigma A) - A_{EI}}{A_{EI}} \times C_{EI} \times V_{EI} \times 100 \times \frac{W}{W}
\]

Which FAME content has unit in %wt, ΣA is the total peak area of methyl ester. A_{EI} is the peak of methyl heptadecanoate which is used as internal standard, C_{EI} is the concentration of methyl heptadecanoate solution (mg/ml), V_{EI} is the volume of methyl heptadecanoate solution (ml), and W is the weight in milligram of sample.

RESULTS AND DISCUSSION

Optimization of esterification step

The experimental designs with code variables, experimental and predicted %FFA were given in Table 3. The multiple regressions were obtained by employing a least square technique to predict quadratic polynomial model for the FFA content. This regression model was tested using analysis of variance for residuals minimization and revealed that the predicted response model was statistically
significant. The coefficient of multiple correlations ($R^2$) in this step had value of 0.973. The high correlation coefficient indicated that the model was suitable to represent the relationship among the studied variables. The predicted model for %FFA ($Y$) in term of code factor was shown in Equation (6).

$$Y = 17.406 - (5.474 \times M) - (7.264 \times C) - (0.114 \times T) - (0.052 \times MM) + (2.187 \times CC) + (2.481 \times 10^5 \times TT) + (0.055 \times MC) + (0.043 \times MT) + (0.019 \times CT)$$

(6)

The response surface plots were shown in Figure 1. Figure 1(A, B and C) was surface plot showing the optimal condition between independent variables in different fixed parameters. As seen in Figure 1(A), the FFA content reduced to less than 2 %wt with increasing methanol to oil molar ratio and $H_2SO_4$ concentration. It indicated FFA content came to reduce by using 1.2:1-2.2:1 of methanol to oil molar ratio and 0.3-1.8 %wt $H_2SO_4$ amount. In case of FFA content, Figure 1(B), FFA content came to reduce by using 1.7:1-2.2:1 of methanol to oil molar ratio and reaction time 40-140 min. Figure 1(C), the FFA content came to reduce by using 0.2-1.8 %wt $H_2SO_4$ amount and reaction time between 50-140 min. When combination the each of surface plots it got to the range of optimum condition. The result got 1.7:1-2.2:1 of methanol to oil molar ratio, 0.3-1.8 %wt $H_2SO_4$ amount and 50-140 min reaction time. After that we selected the optimum condition, it showed 2.2:1 methanol to oil ratio, 0.5 %wt $H_2SO_4$ amount, 60 min reaction time were optimum condition. This optimum condition could reduce FFA content in CPO to 1.54 %wt.

| Table 3. CCD arrangement of code level in esterification and transesterification step. |
|-----------------------------------------------|--------------------|---------------------|---------------------|
| Treatments | M  | C    | T   | Free fatty acid (%FFA) | Fatty acid methyl ester (%FAME) | |
|             | Experimental | Predicted | Experimental | Predicted | |
| 1           | -1 | -1   | -1  | 5.49 | 5.22 | 52.07 | 49.97 |
| 2           | -1 | -1   | 1   | 1.67 | 1.79 | 46.69 | 46.24 |
| 3           | -1 | 1    | -1  | 3.79 | 3.53 | 73.01 | 72.62 |
| 4           | -1 | 1    | 1   | 1.42 | 1.24 | 74.57 | 73.75 |
| 5           | 1  | -1   | -1  | 2.09 | 2.19 | 90.54 | 91.63 |
| 6           | 1  | -1   | 1   | 1.18 | 1.36 | 91.12 | 91.86 |
| 7           | 1  | 1    | -1  | 0.75 | 0.56 | 91.34 | 92.07 |
| 8           | 1  | 1    | 1   | 0.68 | 0.86 | 94.73 | 97.16 |
| 9           | -1.68 | 0    | 0   | 2.70 | 2.93 | 35.03 | 37.43 |
| 10          | +1.68 | 0    | 0   | 0.49 | 0.07 | 94.39 | 92.10 |
| 11          | 0   | -1.68 | 0   | 4.26 | 4.00 | 64.36 | 65.25 |
| 12          | 0   | +1.68 | 0   | 2.09 | 2.16 | 89.52 | 88.73 |
| 13          | 0   | 0    | -1.68 | 2.65 | 2.91 | 90.29 | 90.98 |
| 14          | 0   | 0    | +1.68 | 0.74 | 0.29 | 92.72 | 92.12 |
| 15          | 0   | 0    | 0   | 1.66 | 1.54 | 91.66 | 91.36 |
| 16          | 0   | 0    | 0   | 1.50 | 1.54 | 90.46 | 91.36 |
Figure 1. The response surface plots showing the effect of; (A) methanol to oil molar ratio and H$_2$SO$_4$ concentration, (B) methanol to oil molar ratio and reaction time (min) and (C) H$_2$SO$_4$ concentration and reaction time (min).

**Optimization of transesterification step**

The experimental designs with code variables, experimental and predicted %FAME were given in Table 3. The multiple regressions were obtained by employing a least square technique to predict polynomial model for the %FAME. This regression model was tested using analysis of variance for residuals minimization and revealed that the predicted response model was statistically significant with a coefficient of multiple correlations ($R^2$) in value of 0.995. The high correlation coefficient indicated that the
model was suitable to represent the relationship among the studied variable. The predicted model for %FAME (Y) in terms of code factor was shown in Equation (7).

\[
Y = -22.613 + (20.698 \times M) + (69.639 \times C) - (0.149 \times T) - (1.047 \times MM) - (20.374 \times CC) \\
+ (0.0007432 \times TT) - (3.701 \times MC) + (0.011 \times MT) + (0.081 \times CT)
\]  

(7)

The response surface plots were shown in Figure 2(A, B and C). That figure was surface plot showing the optimal condition between independent variables in different fixed parameters. As seen in Figure 2(A) it showed the amount of FAME product at more than 90% with using 3:1-11:1 of methanol to oil molar ratio and 1.0-1.8 %wt KOH concentration. In case of Figure 2(B), the suitable condition period was 6:1-11:1 of methanol to oil molar ratio and 40-140 min reaction time. Figure 2(C), the suitable condition range was 0.8-1.8 %wt KOH and it got 40-140 min reaction time. When combination the each surface plot to get the range of optimum condition it got 6:1-11:1 of methanol to oil molar ratio, 1.0-1.8 %wt KOH concentration and 40-140 min reaction time. After that, we selected the optimum condition, it showed 7:1 methanol to oil molar ratio, 1.2 %wt KOH concentration, 70 min reaction time. This optimum condition gave 96.24 % of FAME.

![Figure 2](image-url)

**Figure 2.** The response surface plot showing the effect of; (A) methanol to oil molar ratio and KOH concentration, (B) methanol to oil molar ratio and reaction time (min) and (C) H$_2$SO$_4$ concentration and reaction time (min).
CONCLUSIONS

The optimum conditions for biodiesel production were determined with the aid of the central composite design (CCD). The optimum conditions in the first step were found to be as follows 2.2:1 of methanol to oil molar ratio, 0.5 %wt \( \text{H}_2\text{SO}_4 \) and 60 min of reaction time with temperature at 60 \(^\circ\)C. These conditions can reduce FFA from 6.58 %wt to 1.54 %wt which is work complied in requirements to less than 2 %wt. The second step were 7:1 of methanol to oil molar ratio, 1.2 %wt KOH and 70 min reaction time with temperature at 60 \(^\circ\)C. The percentage of fatty acid methyl ester content (FAME) from this optimized condition was 96.57 %.

REFERENCES


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