Effect of choline hydroxide catalyst in the production of methyl ester from crude palm oil

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Abstract. Ionic liquids as catalysts are very potentials for transesterification reactions for biodiesel synthesis. Choline hydroxide (ChOH) has a better catalytic reaction than other ionic liquids because during the reaction takes a shorter reaction time and only requires a small dose of catalyst, the conditions required to produce biodiesel with very high yields. Determination of the optimum conditions for methyl esters resulting from the transesterification reaction of crude palm oil (CPO) using response surface methodology (RSM). The experimental design used three variables, the use of catalyst dose, the molar ratio of crude palm oil (CPO) to methanol and reaction time. Optimal conditions showed the highest methyl ester content was 99.45% at 60 °C, the molar ratio of methanol: CPO 12: 1 and catalyst dose of 3% and a time of 60 minutes. The final product met the selected biodiesel fuel properties by European Standard (EN) 14214. ChOH showed high potential to be used as a low-cost, easy to prepare and high-performance catalyst for biodiesel synthesis.

1. Introduction

Biodiesel is generally produced by the transesterification reaction of the oil with alcohol in the presence of a catalyst, to produce mono-alkyl esters and glycerol, which is then separated and purified [1]. The most common base catalysts used in the biodiesel industry are potassium hydroxide (KOH) and sodium hydroxide (NaOH), which in addition to being cheap, are also easy to handle in transportation and storage and are therefore preferred by small producers [2]. However, there are several problems in the use of these base catalysts, including high energy requirements, difficulties in recovering from glycerol after a reaction, soap formation, and difficulty separating in biodiesel purification [3,4,5].

Ionic liquids have been successfully used as catalysts in biodiesel production by transesterification with good performance, higher conversion, and selectivity in biodiesel production and glycerol conversion [6]. In this study, Reddy et al., (2014) conducted an experiment on biodiesel synthesis from Jatropha curcas oil using liquid ionic liquid namely choline hydroxide (ChOH) and choline imidazolium (ChIM) as catalysts and produced a yield of 95% [7]. In this study, Fan et al., (2013) have conducted an experiment that shows the use of alkaline ionic liquids as catalysts by transesterification for synthesis of soybean oil-based biodiesel with alcohol in the form of methanol, where ionic choline hydroxide...
(ChOH) has a yield of 95% in the absence of soap formation and it has been said that ionic liquids are interesting to explore.

In the production of biodiesel, choline hydroxide is used to produce biodiesel as a catalyst. Choline hydroxide (ChOH) catalysts exhibit better catalytic activity compared to other alkaline ionic liquid catalysts [8]. The focus of this research is about the use of choline hydroxide catalysts and exploring optimal conditions using the RSM and CCD methods in the production of CPO-based biodiesel by transesterification.

2. Method

2.1 Material

The raw materials used are crude palm oil (CPO) obtained from PT Perkebunan Nusantara IV (PTPN IV) which is a State-Owned Enterprises (SOE) concerned in the agro-business field. PTPN IV cultivate plantations and oil palm processing. Methanol (CH$_3$OH) $\geq$ 99.99% and choline hydroxide (ChOH) $\geq$ 99% as powder collected from Sigma-Aldrich.

2.2 Transesterification reaction

The Transesterification reaction is carried out by the stirring speed 400 rpm [9] and a constant temperature of 70°C with process variables as follows a dose of catalyst, the molar ratio of methanol: CPO and reaction time. CPO with a certain amount of weight is weighed and followed by the preparation of methanol and a catalyst ChOH. CPO and methanol were mixed at a specific molar ratio in a flask equipped with a reflux condenser, thermometer, and stirrer. Afterward, ChOH was added and the mixture was stirred and heated using a hot plate till a constant temperature was reached. After that, the mixture was separated using a separator funnel until 2-3 layers were formed, then washed until the washed water is clear. Analysis product methyl ester used GC-MS.

2.3 Experimental design

Factors affecting the reaction such as the molar ratio of methanol and CPO, reaction time and a dose of catalyst were systematically analyzed by response surface methodology (RSM) with central composite design (CCD). The code level and the combination of research treatments obtained from the STATISTICA Trial Version program. The level of code and a combination of the research can be seen in tables 1 and 2 [10]. The design of the model equations is as follows:

$$Y = \beta_0 + \beta_1 \chi_1 + \beta_2 \chi_2 + \beta_3 \chi_3 + \beta_4 \chi_4 \chi_2 + \beta_5 \chi_5 \chi_2 + \beta_6 \chi_6 \chi_3 + \beta_7 \chi_7 \chi_3 + \beta_8 \chi_8 \chi_2 + \beta_9 \chi_9 \chi_2 + \beta_{10} \chi_{10} \chi_2 + \varepsilon$$

(1)

| Variables                  | Symbols | Levels   |
|----------------------------|---------|----------|
| Catalyst Dosage (w/w)      | X$_1$   | -1.673   |
|                            |         | -1       |
|                            |         | 0        |
|                            |         | 1        |
|                            |         | 1.673    |
| Molar Ratio Methanol: CPO  | X$_2$   | 4:1      |
|                            |         | 6:1      |
|                            |         | 9:1      |
|                            |         | 12:1     |
|                            |         | 14:1     |
| Reaction Time (min)        | X$_3$   | 40       |
|                            |         | 60       |
|                            |         | 90       |
|                            |         | 120      |
|                            |         | 140      |

Table 1. Code level central composite design [10].
Table 2. Central composite design for three variables [10].

| No | The dose of Catalyst (w/w) | Molar Ratio Methanol: CPO | Reaction Time (minute) |
|----|----------------------------|--------------------------|------------------------|
| 1  | -1                         | -1                       | -1                     |
| 2  | -1                         | 1                        | 1                      |
| 3  | 1                          | -1                       | 1                      |
| 4  | 1                          | 1                        | -1                     |
| 5  | 0                          | 0                        | 0                      |
| 6  | -1                         | -1                       | 1                      |
| 7  | -1                         | 1                        | -1                     |
| 8  | 1                          | -1                       | -1                     |
| 9  | 1                          | 1                        | 1                      |
| 10 | 0                          | 0                        | 0                      |
| 11 | -1.673                     | 0                        | 0                      |
| 12 | 1.673                      | 0                        | 0                      |
| 13 | 0                          | -1.673                   | 0                      |
| 14 | 0                          | 1.673                    | 0                      |
| 15 | 0                          | 0                        | -1.673                 |
| 16 | 0                          | 0                        | 1.673                  |
| 17 | 0                          | 0                        | 0                      |

3. Results and discussion

3.1. Effect of process variables to % yield

Following the experimental results data in a central composite design and the combination of the research can be seen in table 3.

Table 3. Yield methyl ester in central composite design [10].

| No | The dose of Catalyst (w/w) | Molar Ratio Methanol: CPO | Reaction Time (minute) | % Yield  |
|----|----------------------------|--------------------------|------------------------|----------|
| 1  | -1                         | -1                       | -1                     | 98.8095  |
| 2  | -1                         | 1                        | 1                      | 87.9123  |
| 3  | 1                          | -1                       | 1                      | 98.4424  |
| 4  | 1                          | 1                        | -1                     | 98.7289  |
| 5  | 0                          | 0                        | 0                      | 98.7911  |
| 6  | -1                         | -1                       | 1                      | 68.0423  |
| 7  | -1                         | 1                        | -1                     | 99.4449  |
| 8  | 1                          | -1                       | -1                     | 83.8399  |
| 9  | 1                          | 1                        | 1                      | 97.8193  |
| 10 | 0                          | 0                        | 0                      | 98.7911  |
| 11 | -1.673                     | 0                        | 0                      | 62.9673  |
| 12 | 1.673                      | 0                        | 0                      | 81.3721  |
From Experimental results processed using STATISTICA trial version program to get the parameters from the model equation that will provide estimates of the effect of variables to the % yield. Statistical analysis to determine the significance of the influence of variables can be seen in Table 4.

Table 4. Regression coefficients.

| Model Parameter | Parameter estimate | Standard error | Computed t-value | P-value |
|-----------------|--------------------|----------------|------------------|---------|
| Intercept       | 95.7845            | 24.0102        | 3.9893           | 0.0104  |
| X<sub>1</sub>   | 8.4867             | 6.5630         | 1.2931           | 0.2525  |
| X<sub>2</sub>   | 6.8435             | 6.5630         | 1.0427           | 0.3448  |
| X<sub>3</sub>   | -16.9309           | 6.5630         | -2.5798          | 0.0495  |
| X<sub>1</sub><sup>2</sup> | -5.7493           | 9.8766         | -0.5821          | 0.5858  |
| X<sub>2</sub><sup>2</sup> | 2.6506            | 9.8766         | 0.2684           | 0.7991  |
| X<sub>3</sub><sup>2</sup> | -13.8176           | 9.8766         | -1.3990          | 0.2207  |
| X<sub>1</sub>X<sub>2</sub> | -8.2799           | 8.5571         | -0.9676          | 0.3777  |
| X<sub>1</sub>X<sub>3</sub> | 14.4991           | 8.5571         | 1.6944           | 0.1510  |
| X<sub>2</sub>X<sub>3</sub> | 7.9653            | 8.5571         | 0.9309           | 0.3947  |

Based on the results of the statistical analysis in table 4, the % yield equation model is obtained as follows.

\[
Y_{\text{yield}} = 95.7845 + 8.4867X_1 + 6.8435X_2 - 16.9309X_3 - 5.7493X_1^2 + 2.6506X_2^2 - 13.8176X_3^2 - 8.2799X_1X_2 + 14.4991X_1X_3 + 7.9653X_2X_3
\]  

(2)

3.2. Effect of catalyst dose variable interaction with molar ratio to % biodiesel yield

Results of experimental modeling with the 3D surface plot was made to produce a response % yield with two other variables, the plot can be seen in figures 1 to 3 below. Figure 1 showed the relationship between % yield of the dose of the catalyst and the molar ratio of methanol: CPO this figure shows that catalyst dosage gives a greater effect than the molar ratio. There are several areas optimum based on figure 1 above, catalyst dosage 3.5% (w/w) with a molar ratio reactant 12:1 to 14:1 will produce a yield over 98%. Other optimum area show of catalyst dosage of 4.5-5.5% (w/w) but followed with a molar ratio of reactants were lower by 4:1 will produce yield methyl ester 93%.
5.3. Effect of catalyst dose variable interaction with reaction time on biodiesel yield %

Figure 1. Surface response plot % biodiesel yield for catalyst doses and reactant molar ratios.

Figure 2. Plot surface response % biodiesel yield for catalyst and doses reaction time.

Whereas in figure 2 can be seen the relationship between % yield of the catalyst dosage and reaction time, this picture shows that the use of catalysts ChOH will be optimum with shorter time, the longer reaction time will reduce % yield of the methyl ester, the use of a catalyst ChOH provide advantages in biodiesel transesterification reaction. Catalyst dosage and reaction time have a significant effect on the % yield of the methyl ester. The optimum area occurs at doses catalysts 2.5-5% (w/w) with a reaction time of up to 90 minutes will produce a yield of methyl ester over 98%. 
3.4. Effect of interaction of molar ratio variables with reaction time on % biodiesel yield

![Graph showing the interaction of variables with reaction time on biodiesel yield.](image)

Figure 3. Surface response plot % biodiesel yield for reactant molar ratio and reaction time.

Figure 3 can be seen the relationship between % yield on the molar ratio of methanol: CPO and reaction time. Figure 3 also shows that the molar ratio fluctuates, rising at 6:1 and then decreased at 9:1 and then increased again to 14:1 yield of methyl ester over 96% with the reaction time of 40-90 minutes. The longer time reaction can decrease the yield.

3.5. Methyl esters properties
To assess the quality of the final product, it was evaluated according to European biodiesel standard (EN) 14214 (Table 5). It was found that the final product meets all the tested parameters (ester content, density, viscosity) by EN 14214.

| Fuel Properties     | Unit    | This Work | EN 14214 |
|---------------------|---------|-----------|-----------|
| Ester content       | %w/w    | 99.90     | ≥ 96.5    |
| Density             | kg/m³   | 862       | 860-900   |
| Viscosity kinematic | mm²/s   | 3.2       | 3.5-5.0   |

4. Conclusion
CPO as raw material to produce biodiesel without going through the pre-treatment (refined) can be used with the aid of a basic catalyst ionic liquid choline hydroxide (ChOH) and give % yield relatively good. The basic ionic liquid ChOH possessed better basicity in methanol solution, which promoted the catalytic performance. The highest content of methyl ester is 99.45% at 60 °C with a molar ratio of methanol to CPO 12:1 and the catalyst dosage 3% (w/w) at 60 minutes. This shows that the ChOH catalyst has very good catalytic properties where the equilibrium reaction can be achieved in a short time so that it can produce high product yields.
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