Synthesis of Biodiesel Using Carbon-Based Solid Catalyst

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Abstract

Biodiesel is mostly made from trans-esterification reaction using homogenous catalysts. Problems related to homogenous catalysts are the difficulty to separate the final product and the toxic that the waste contains. To prevent this negative effect, it is suggested to use heterogeneous catalysts.

Several studies related to heterogeneous catalysts have been studied by researchers since the use of heterogeneous catalysts instead of homogeneous ones can be expected to eliminate the problems associated with homogeneous catalysts. The solid-based catalysts are easily regenerated and have a less corrosive nature, leading to safer, cheaper, and more environment-friendly operations.

In this paper, the trans-esterification of palm oil to biodiesel was studied using KOH loaded on activated carbon (K-AC) as heterogeneous catalyst. Reaction parameters such as temperature, percentage of catalyst amount, and molar ratio of oil to methanol were optimized to reach the highest conversion. Iodometry method was used to determine bonding glycerol in final product. The highest conversion of glycerol, 22.71%, was obtained by using 3% catalyst amount at 60 °C temperature and 1:6 molar ratio of palm oil to methanol. The low conversion was probably due to the catalyst’s pore size which is not large enough, causing only a few triglycerides able to pass through the pore and react with KOH.

Keywords: Biodiesel; Heterogeneous catalyst; Trans-esterification; KOH loaded activated carbon

1. Introduction

Biodiesel is defined as methyl ester which is derived from trans-esterification reaction of vegetable oils, animal fats and used oil from food industry using alcohol in the presence of catalyst. The idea of using vegetables oils as fuel for engine has been known for more than 100 years ago, but it was not widely used because refined crude oil were still cheaper and more appropriate as fuel or diesel fuel (Mittelbatch and Remschmidt, 2004).

Nowadays, crude oil price is increased and the resource of fossil oil is limited. Furthermore, continued and increasing use of fossil oil will worsen the green house effect caused by CO$_2$. It has been a new concern to find renewable energy that could lower the dependence of crude oil, reduce greenhouse gas emissions, and would not deliver any toxic effect to environment. Biodiesel is noteworthy for its similarity to petroleum based diesel but with less worse impact.
There are several materials which can be used to make biodiesel and one of them is palm oil. Palm oil is produced from palm mesocarp, which is characterized by high content of palmeat acid and oleic acid. The advantages of using palm oil as a raw material are the large amount of oil palm plantations in Indonesia and the cheaper price than other edible oils (Susila, 2004).

Biodiesel is mostly made from reacting palm oil and alcohol with the presence of homogenous catalysts. Problems related to homogenous catalysts are the difficulty to separate the final product and the toxic that the waste contains. To prevent this negative effect, it is suggested to use heterogeneous catalysts (Di Serio et al, 2007). The solid-based catalysts are easily regenerated and have a less corrosive nature, leading to safer, cheaper, and more environment-friendly operations.

KOH loaded on activated carbon (K-AC) is able to accelerate the trans-esterification reaction because of its active sites that reacts with triglyceride molecules. The advantages of using activated carbon as a catalyst support are its sufficient surface area, inert, and stable in high pressure or temperature. As a catalyst support, activated carbon pore size should be large enough to react with triglyceride molecule (approximation of molecular size is 2-4 nm).

2. Materials and Methods

2.1. Materials

Refined palm oil (Bimoli) was used as a raw material for biodiesel production.

2.2. Trans-esterification of palm oil

Trans-esterification reaction of palm oil was carried out in a three-neck round-bottomed flask (250 ml) equipped with a condenser, magnetic stirrer, and temperature indicator. A known amount of palm oil was added to reactor then heated to the desired temperature (60°C). Methanol was also heated to the desired temperature, then added to the reactor filled already by palm oil. The temperature of the mixture was maintained isothermal. A known amount of catalyst was added to the mixture. The molar ratio of methanol to oil used in this study was 4, 6, and 8. The trans-esterification reaction was carried out for 1-4 hours. After the reaction time, the solution was centrifuged for 10 minutes. Glycerol was in the bottom layer, separated with pipettes from the methyl ester layer.

2.3. Determination of biodiesel conversion

The glycerol produced from the trans-esterification was analyzed by iodometry method to determine the bonding glycerol. The conversion of biodiesel was determined using the following equation
\[ Conversion = \frac{Glycerol_{bonding\ in\ raw\ material} - Glycerol_{bonding\ in\ sample}}{Glycerol_{bonding\ in\ raw\ material}} \times 100 \] (1)

3. Results and discussion

3.1. Effect of the amount of catalyst

The amount of catalyst added to the mixture was varied from 1, 3 and 5% by weight based on the amount of palm oil. The conversion of palm oil to glycerol was increased from 19.9% at 1% K-AC to 22.71% at 3% (Table 1). The increase was due to an increase in the number of active basic sites in the reaction. 5% amount of catalyst added to the mixture did not show a significant increase. According to Le Chatelier principle, a reversible reaction is limited by equilibrium condition. Increasing the amount of catalyst would not affect the conversion if the catalyst has provided sufficient basic sites and the reaction has reached its equilibrium.

Table 1
The effect of different process variables on the conversion of glycerol.

<table>
<thead>
<tr>
<th>Palm oil : Methanol ratio</th>
<th>Temperature (°C)</th>
<th>Amount of catalyst (%)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:4</td>
<td>60</td>
<td>3</td>
<td>21.74</td>
</tr>
<tr>
<td>1:6</td>
<td>60</td>
<td>3</td>
<td>22.71</td>
</tr>
<tr>
<td>1:8</td>
<td>60</td>
<td>3</td>
<td>22.31</td>
</tr>
<tr>
<td>1:6</td>
<td>50</td>
<td>3</td>
<td>20.61</td>
</tr>
<tr>
<td>1:6</td>
<td>55</td>
<td>3</td>
<td>19.61</td>
</tr>
<tr>
<td>1:6</td>
<td>60</td>
<td>1</td>
<td>19.99</td>
</tr>
<tr>
<td>1:6</td>
<td>60</td>
<td>5</td>
<td>20.20</td>
</tr>
</tbody>
</table>

3.2. Effect of temperature

The temperature of reaction was varied from 50, 55, and 60° C. The highest conversion was obtained by the reaction carried out at 60° C (Table 1). This satisfies the Arrhenius principle, saying the increase of reaction rate is parallel with the increase of temperature.
Trans-esterification reaction using solid catalyst can be assumed as a pseudo-homogenous reaction. Due to the presence of stirrer, the resistance of mass transfer from liquid to solid can be neglected, therefore reactant and catalyst were in the same phase. Methanol to oil ratio was set excessed so the concentration of methanol was constant.

In order to predict the rate of reaction, the reaction order is guessed by finding the linear relation between the conversion and time through integral method (Levenspiel, 1999). For the first, it is assumed that the order reaction is 1. The relation between $-\ln(1-x)$ and $t$ are given in fig. 1, 2, and 3.

![Fig. 1. $-\ln(1-x)$ as a function of $t$ at 50 °C](image1)

![Fig. 2. $-\ln(1-x)$ as a function of $t$ at 55 °C](image2)
It is implied from fig. 1, 2, and 3 that the relation between $-\ln(1-x)$ and $t$ is approaching linearity. Therefore, the first assumption is correct. From the linearization of the graphic, an equation is obtained as correction factor to find the actual value of rate reaction. The rate reactions for each temperature are: $k'_{50}=0.1081$; $k'_{55}=0.1063$; dan $k'_{60}=0.12395$ (hour$^{-1}$). (gram catalyst$^{-1}$). The relative errors for each equation are 3.42%, 2.66% dan 6.3%.

3.3. Effect of reactant ratio

Reaction was carried out in the presence of 3% the amount of catalyst at 60 °C. The highest conversion was obtained by palm oil to methanol ratio 1:6 (table 1). Basically, trans-esterification is a reversible reaction. The purpose of methanol to palm oil ratio was set excessively from its stoichiometry need is to alter the equilibrium towards product side. Yet, palm oil to methanol ratio 1:8 did not obtain a significant higher conversion because the equilibrium was already reached.

4. Conclusion

KOH loaded on activated carbon (K-AC) as a heterogeneous catalyst can be used as solid based catalyst for biodiesel production from trans-esterification of palm oil. The operating condition to obtain the highest conversion was: amount of catalyst 3%, methanol to oil ratio 6, and the reaction temperature at 60°C.

Acknowledgements
References

