The Contribution Of Heterogeneous And Homogeneous Catalysts Towards Biodiesel Quality

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Abstract. Homogeneous catalysts and heterogeneous catalysts are two types of catalysts used in the transesterification reaction process to produce biodiesel. Homogeneous catalysts that are commonly used are NaOH and KOH, while heterogeneous catalysts are CaO, super base CaO and Zeolite. This research was conducted to determine the contribution of catalysts NaOH, CaO, super base CaO, and zeolite to the quality of biodiesel produced from bulk palm oil. The reaction process is carried out in a Stirred Tank Flow Reactor equipped with a condenser. The results showed that the use of homogeneous catalysts could increase the acquisition of biodiesel but generally triggered high acid levels in the reaction products. Whereas heterogeneous catalysts can reduce biodiesel acid numbers, although the acquisition of biodiesel is lower than homogeneous catalysts.

1. Introduction

Biodiesel is an ester compound that binds to an alkyl group in the form of methyl, ethyl propyl or butyl. But until now, the ester that binds to alkyl in the form of methyl is still the main choice. This is because methanol is more reactive than other alkyl source compounds such as ethanol, propanol and butanol. In addition, the use of the reaction temperature is significantly lower when methanol is used compared to other compounds. This condition is a major consideration in terms of energy if biodiesel is to be mass produced (manufacturing).

A catalyst is a substance that can accelerate the rate of chemical reactions. In general, catalysts used in chemical reactions are of three types, namely homogeneous catalysts, heterogeneous catalysts and enzymes (Nasikin and Bambang 2016). Generally, conventional biodiesel is produced using homogeneous catalysts NaOH and KOH, but this process requires a stage of product separation. (Devitria, 2013).

Bulk oil (palm oil) and waste cooking oil are two types of vegetable oil that are very potential to be used as raw materials for making biodiesel because they have several advantages. The use of used cooking oil as raw material for biodiesel must consider the physical and chemical properties of used cooking oil. Cooking oil that has undergone a frying process repeatedly increases the content of free fatty acids due to the occurrence of hydrolysis reaction during frying.

Zeolite is a catalyst that is also often used in making biodiesel because it has important preparations that cannot be found in conventional amorphous catalysts. Zeolites have hollow structures and cavities are usually filled with water and cations that can be exchanged and have a certain pore size. Therefore, zeolites can be used as filters, ion exchangers, absorbent materials, and catalysts (Sutarti, 1994). The working power of zeolite as a catalyst can be enlarged by activating the zeolite first.

In this research, the production of biodiesel based on bulk palm oil using catalysts NaOH, zeolite and CaO superbasa. NaOH catalyst is a homogeneous catalyst group, while zeolite and CaO superbasa are heterogeneous catalyst groups. In this study the performance of the two catalysts will be compared based on their ability to convert the fatty acids in used cooking oil to esters and the characteristics of the biodiesel produced.
2. Methodology

Materials: The materials used as samples in this study are bulk palm oil and waste cooking oil. The chemicals used are aquades, NaOH, methanol, CaO Super Bases, zeolites, Phenol Phthalein indicators. The tools used in this study include glass reactors, picnometers, ostwald viscometers, a set of titration tools, ovens, electric baths, pH meters, condensers, thermometers, analytical balances, measuring vessels, erlenmeyer flasks of various sizes, plastic containers, pipettes various sizes and stirring rods.

Preparation of Catalyst:

CaO superbase: To obtain a superb CaO catalyst, 12 grams of CaO was dipped in a solution of ammonium carbonate concentrating 0.12 g / mL, as much as 171.5 mL, stirred for 30 minutes and filtered. The collected solids are heated at 110 °C, and calcined at 700 °C for 15 hours. After calcining, the CaO solid is allowed to reach 250 °C and is put into a desiccator to prevent contact between the surface of the catalyst and water vapor which results in decreased strength of the catalyst base. (Lilianti, 2018)

Zeolite: Activation is done by weighing zeolite put into a bottle, then dropped with H2SO4 and then homogenized for 30 minutes. After that it is allowed to stand for 24 hours.

NaOH: Weigh 4 grams NaOH, then dissolve with distilled water. Enter into 1000 ml measuring flask, then add distilled water to the boundary mark. NaOH 0.1 M solution is ready to use.

Biodiesel Production: The transesterification device circuit consists of a stirred reactor, water bath, thermocouple, and condenser. into the reactor, heated to a temperature of 65 °C. The solution is mixed into palm oil and the reaction time starts to be calculated. During the reaction it is stirred at 200 rpm and the reactant temperature is controlled using a temperature controller. The reaction is stopped after the desired reaction time has been reached after which the mixture is poured into a separating funnel, then allowed to stand for ± 12 hours until it forms a separate layer of methyl ester and glycerol. Then wash the methyl esters using distilled water at 50 °C. The mixture is homogenized and allowed to stand for a few moments to form 2 layers. The bottom layer of water is removed and the washing is repeated several times until the neutral methyl ester has been obtained. Then the methyl ester is then put into the oven at 110 °C for 1 hour to remove the remaining water content. Furthermore, an analysis of biodiesel quality test was carried out.

3. Result and Discussion

Based on the data in Table 1, it was produced that the research carried out twice was run with the amount of bulk palm oil, methanol, and catalysts of super base CaO, Zeolite, and NaOH which produced biodiesel and glycerol.

| Catalysts       | Run | Bulk Palm Oil (ml) | Methanol (ml) | NaOH (g) | Biodiesel (ml) | Glycerol (ml) | Yield (%) |
|-----------------|-----|--------------------|---------------|----------|----------------|---------------|-----------|
| NaOH            | I   | 347,79             | 121,95        | 0,34     | 259            | 39            | 74,47     |
|                 | II  | 347,79             | 121,95        | 0,34     | 256            | 40            | 73,60     |
| Zeolite         | I   | 347,79             | 121,95        | 0,34     | 342            | 26            | 98,33     |
|                 | II  | 347,79             | 121,95        | 0,34     | 340            | 28            | 97,76     |
| CaO superbase   | I   | 347,79             | 121,95        | 0,34     | 259            | 30            | 74,47     |
The use of catalysts is influenced by the amount of yield. In Table 1 presented biodiesel yield data obtained from the production process using zeolite catalysts were 98.33% and 97.76%, respectively. This result is higher than the yield of biodiesel produced using NaOH catalysts which is 74.47% and 73.60% and yields of CaO superbase catalysts 74.47% and 73.60%.

Biodiesel Characteristics Test
The transesterification biodiesel is then analyzed to determine the nature of the biodiesel. The results of the analysis are then compared with the standards set by SNI. The analysis included water content, density at 400°C, viscosity, acid number, iodine number, and saponification number.

Density: From Figure 1 shown it can be seen that the density with a Zeolite catalyst is 916.912 kg/m³ greater than the density with a CaO super base catalyst 906 kg/m³ and the density of the NaOH catalyst is 880 kg/m³. The density analysis is done using a 25 ml pycnometer, from the graph also shows that the biodiesel density using the NaOH catalyst is lower than the biodiesel density using a zeolite and CaO super base catalyst. When compared to densities based on SNI-04-7182-2015 where the price of density is 850-890 kg/m³. So, it can be seen in this study that the biodiesel characteristics meet the requirements using NaOH catalyst, while the density using Zeolite and CaO super base catalysts does not meet the biodiesel characteristics based on SNI.

Figure 1. Comparison graph of the biodiesel characteristics of each catalyst to its density.

Viscosity: Biodiesel viscosity analysis was carried out using the Ostwald viscometer. From Figure 2 above, pay attention to the viscosity of each biodiesel with different catalysts, the viscosity of biodiesel with zeolite catalyst 36.4; 37.9 cSt and super alkaline CaO catalyst viscosity 37.3; 40.4 cSt higher than 5.04 NaOH catalyst viscosity; 5.66 cSt. When compared with the characteristics of biodiesel based on SNI-04-7182-2015, where the price of viscosity is 2.3-6.0 cSt, the biodiesel results of this study using NaOH catalyst already meet the requirements of biodiesel characteristics while the zeolite catalyst and CaO super base catalyst are not meet the requirements of biodiesel characteristics.
Acid Number: Based on Figure 3 below, it can be seen that the acid number using the NaOH catalyst is 0.70; 0.22 mg KOH / g and super base CaO catalyst 0.22; 0.59 mg KOH / g lower than the number of biodiesel acids using zeolite catalyst. According to SNI-04-7182-2015, the maximum acid number is 0.8 mg KOH / g of oil. So the acid numbers in this study for the NaOH and CaO super base catalysts are still eligible while the zeolite catalyst is not eligible.

Saponification value: From figure 4 below, it can be seen that the saponification numbers in biodiesel use either NaOH catalyst 254.58; 263.16 mg KOH / gram, zeolite catalyst 264.59; 268.89 mg KOH / gram, and super base CaO catalyst 266.03; 271.75 mg KOH / gram. Characteristics of biodiesel compounding rates on each catalyst are in accordance with the requirements for biodiesel quality according to SNI-04-7182-2006, acid number for a maximum of 500 mg KOH / gram.
Figure 4. Comparison graph of saponification numbers

Iodine Value: From Figure 5 below shows the iodine number of Cao super base catalyst 6.41; 8.86 g I2 / 100g. Higher than the biodiesel iodine number of NaOH catalyst 0.30; 3.17 g I2 / 100g and iodine biodiesel zeolite catalyst 6.23; 5.79 g I2 / 100g. Then, if the iodine number of biodiesel with the catalyst used is compared with the characteristics according to SNI-04-7182-2015 which has a max value of 115 g I2 / 100g, then the iodine value for biodiesel in this study meets the requirements.

Figure 5. Comparison graph of iodine numbers

4. Conclusion
The quality of biodiesel from bulk palm oil is strongly influenced by the type of catalyst used. The yield of biodiesel produced from a homogeneous catalyst (NaOH) tends to be lower than the yield obtained from processes using heterogeneous catalysts (zeolite and CaO superbas). However, based on the results of the characteristic test, biodiesel produced from a homogeneous catalyst process generally meets SNI standards. Conversely, biodiesel obtained from heterogeneous catalytic processes still does not fully meet SNI standards.

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