Effectiveness of Heterogenous Catalyst In Biodiesel Production Process: The Use of Zeolite, ZnO and Al₂O₃

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Abstract. One of the most important needs in the biodiesel industry is the availability of catalysts. The catalyst most commonly used in making biodiesel is a homogeneous catalyst. However, the use of this catalyst has a weakness, namely that it is difficult to separate from the reaction mixture so that it will be wasted as waste which can cause environmental pollution. To overcome this, it is necessary to substitute a homogeneous base catalyst with a heterogeneous base catalyst. In this study, biodiesel production was carried out through the transesterification reaction of palm oil and methanol using three types of heterogeneous catalysts, namely zeolite, ZnO, and Al₂O₃. The results showed that the three types of catalysts can be used to become catalysts in the biodiesel production process. Of the three catalysts, the most effective use for biodiesel production from palm oil is the Al₂O₃. The characteristics of the biodiesel produced also meet the quality standards set out in the Indonesian National Standard.

Keywords: Heterogenous catalyst, Biodiesel, Transesterification

1. Introduction

Catalysts have a very important role in industrial processes, where more than 75% of chemical synthesis processes industry are highly dependent on the availability of catalysts. Types of process industries that require catalysts include the fuel, pharmaceutical and chemical industries [1]. Catalyst is a substance that can accelerate the rate of chemical reactions. In a chemical reaction the catalyst undergoes changes both chemically and physically. Therefore, the catalyst can affect the speed of the reaction, even if the reaction is carried out at a low temperature.

In general, catalysts are grouped into two types, namely homogeneous catalysts and heterogeneous catalysts [2]. The two types of catalysts can be organic or inorganic compounds. In the biodiesel industry, the catalysts commonly used are homogeneous catalysts such as NaOH and KOH. The advantage of using a homogeneous catalyst is the trend of the conversion of transesterification which is quite high compared to the use of heterogeneous catalysts, besides that it also has a disadvantage, namely that the catalyst is difficult to separate from the reaction product, and triggers the formation of reactions. -products such as soap, so that the process becomes uneconomical [3]. The advantages of using heterogeneous catalysts are that they are sufficiently available in nature, do not cause side reactions, are easily released from the reaction products, and can be reused after being activated [4].
Some heterogeneous catalysts derived from natural materials and can be used for the biodiesel production process include CaO, zeolite, ZnO and Al2O3. Studies on the use of CaO have been developed, but the use of zeolite, ZnO and Al2O3 has not received much attention. Zeolites have a hollow structure and usually these cavities contain water and cations which can be exchanged and have a certain pore size. Therefore, zeolites can be used as filters, ion exchangers, absorbent materials, and catalysts [5]. The working power of zeolite as a catalyst can be enlarged by activating the zeolite first. ZnO can be used repeatedly and very easy to separate. The use of ZnO can reduce the cost of biodiesel production, because the catalyst separation process and waste treatment are easy to do. Al2O3 has properties as a heat insulator and a good electrical insulator and is resistant to high temperatures so it is often used as a catalyst or solid catalyst support. To determine the effectiveness of using zeolite, ZnO and Al2O3 catalysts in the biodiesel production process, research has been carried out on the biodiesel production process using palm oil as raw material. The chemical and physical properties of the biodiesel produced have been analyzed.

2. Research Method

This research was conducted at the Chemical Technology Laboratory of the Chemical Engineering Study Program, Faculty of Engineering, Universitas Kristen Indonesia Paulus Makassar. The raw material in the form of Crude Palm Oil (CPO) was obtained from the Burau Palm Oil Mill in East Luwu Regency. Chemicals such as methanol, ammonium carbonate, zeolite, ZnO and Al2O3 were purchased from a chemical shop in the city of Makassar. The research stage consisted of three main stages, namely preparation of the catalyst, the transesterification reaction process and testing the characteristics of biodiesel.

Preparation of catalysts: Zeolite catalyst preparation was carried out according to the procedure carried out by [3]. Natural zeolite is crushed, then put into a bottle and dripped with H2SO4 (p). Mixing is done by shaking the bottle containing the zeolite for about 30 minutes, then let it sit for 24 hours. Then it was calcined in a furnace for 2 hours at a temperature of 450 °C. The preparation of the ZnO catalyst was carried out according to the procedure carried out by Hassapour, et all. [6]. The activation process is carried out in a furnace tube by flowing nitrogen gas at 400 °C for 5 hours. For Al2O3 it doesn't need to be processed anymore, Al2O3 purchased from chemical stores is used directly in making biodiesel.

Biodiesel Production Process: Palm oil, methanol, and catalyst were put into the reactor, heated to a temperature of 65 °C. The solution was mixed into palm oil and the reaction time was calculated to reach 2 hours. During the reaction, stirring was carried out at a speed of 200 rpm and the temperature of the reactants was controlled using a temperature controller. The reaction is stopped after reaching the desired reaction time. The mixture is poured into a separating funnel, then allowed to stand until it separates to form a layer of methyl ester and glycerol. The crude biodiesel is washed using distilled water at 50 °C. The mixture is homogenized and allowed to stand for a while to form 2 layers. The underwater layer was removed and the washing was repeated several times until the methyl ester was neutral. After the methyl ester was obtained, then the methyl ester was put in an oven at 110 °C for 1 hour to remove the remaining moisture content. Furthermore, analysis of the quality test for biodiesel is carried out.

Test the Biodiesel Characteristics: Biodiesel characteristic tests were carried out to determine viscosity based on ASTM D 445 test method, acid number with ASTM D 664 test method, and saponification number. The test results are compared with the standards set out in the Indonesian National Standardization Agency (SNI 04-7182-2015-Biodiesel).

3. Result and Discussion
Table 1 shows the yield of biodiesel from the transesterification reaction using three different types of catalyst, although the amount of oil and the amount of methanol are the same for each reaction. The product from the reaction process with the ZnO catalyst obtained biodiesel as much as 295-299 ml (yield 73.45% - 74.45%), this result is the same as that reported by Yulianti C.H., et al [7]. The product from the Al$_2$O$_3$ catalyst process produces 375-380 ml of biodiesel (yield 93.75% - 95.00%), which is higher than the yield reported by Mujihartim et al [8], namely 76.95%. While the yield of the product from the process using 330-340 ml zeolite catalyst (yield 82.50% - 85.00%), was lower than the results reported by Sari Ulfayana, et al, where the yield was 97.79%. The three types of heterogeneous catalysts can be used for the process of making biodiesel. The use of these three catalysts facilitates the separation of biodiesel from glycerin because the reactions of the three do not trigger the saponification reaction as is generally the case in processes using homogeneous catalysts. However, from the three catalysts the highest yield was obtained from the use of Al$_2$O$_3$ catalyst, then zeolite and finally ZnO.

Table 1. Yield of Biodiesel

| Run  | Oil (ml) | Methanol (ml) | Catalyst (gr) | Biodiesel (ml) | Yield (%) |
|------|----------|---------------|---------------|---------------|-----------|
|      |          |               | ZnO | Al$_2$O$_3$ | zeolit | ZnO | Al$_2$O$_3$ | zeolit |           |           |           |
| I    | 400      | 250           | 4   | 4           | 4       | 295 | 380 | 330 | 73,7 | 95 | 82,5 |
| II   | 400      | 250           | 4   | 4           | 4       | 299 | 375 | 340 | 74,7 | 93,75 | 85 |

The characteristics of the biodiesel produced are presented in Table 2. The viscosity of biodiesel produced from the process using an Al$_2$O$_3$ catalyst (5.30 cSt) is lower than the viscosity of biodiesel produced through a process using zeolite and ZnO catalysts. However, the three of them still meet the SNI for Biodiesel because they are in the range of values 2.3 - 6.0 cSt. Likewise with the acid number, the lowest value is obtained from the process using an Al$_2$O$_3$ catalyst (0.38 mg-NaOH / g), but all three of them still meet the SNI Biodiesel because they are in the range of values that are less than the SNI provisions, namely 0.5 mg-NaOH/g.

Table 2. Characteristics of biodiesel

| Biodiesel produce with Catalyst | Viscosity (cSt) | Acid number (mg-NaOH/g) | Iodin number (mg-I$_2$/g) | Saponification number (mg-KOH/g) |
|-------------------------------|----------------|------------------------|--------------------------|----------------------------------|
| ZnO                           | 5.71           | 0.44                   | 56.95                    | 181.78                           |
| Zeolit                        | 5.41           | 0.49                   | 57.08                    | 182.29                           |
| Al$_2$O$_3$                   | 5.30           | 0.38                   | 75.16                    | 179.27                           |

The iodine number of the three reaction products is still lower than the SNI provisions, namely 100 - 115 mg-I$_2$ / g), however this is very much influenced by the oil raw material used. The iodine value from the process using Al2O3 catalyst is closer to the iodine number stipulated by the SNI. For the foam rate characteristics, the saponification rate in the process using an Al$_2$O$_3$ catalyst is lower than the saponification rate in biodiesel produced through a process using zeolite and ZnO catalysts.
Based on Table 3, it is known that the fatty acids that make up biodiesel from palm oil are more dominant saturated fatty acids than unsaturated fatty acids. The saturated fatty acids are Pentadeconoic Acid, Stearic Acid, Heptadecene-8-Carbonic Acid, Myristic Acid, and Hexadecanoic Acid. Meanwhile, unsaturated fatty acids consist of Octadec-9-Enoic Acid (Oleic Acid) and 2,4-Decadienal. The fatty acid groups that make up biodiesel are fatty acids that are included in the long carbon chain, which can provide a better heating calorific value.

4. Conclusion

Based on the research results obtained, it can be concluded that

1. Three types of heterogeneous catalysts used, namely ZnO, zeolite, and Al2O3 can be used as catalysts in the biodiesel production process
2. The use of Al2O3 as a catalyst is more effective than the other two catalysts, because it can produce the highest yield of 94.38% and better characteristics.
3. The quality of biodiesel obtained in this study has met the quality standards for biodiesel according to SNI-04-7182-2015 which has met the standards.

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