Performance of Activated Natural Zeolite/Cu as a catalyst on Degradation of Glycerol into Ethanol Assisted by Ultrasonic

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Abstract. The purpose of this study was to convert glycerol into ethanol using the catalyst of activated natural zeolite/Cu assisted by ultrasonic. The catalyst was characterized using X-Ray Diffraction and BET isotherm adsorption. The degradation process carried out at the temperature of 60 °C and at various time of 1, 2, and 4 hours. The product of glycerol degradation was analyzed using Gas Chromatography. The results showed that the structure of natural zeolite was a mordenite. The BET analysis showed that the surface area of natural zeolite is 99.096 m²/g greater than that of natural zeolite impregnated Cu that is 6.597 m²/g. The total pores, however, a natural zeolite is 0.026 cm³ smaller than that of natural zeolite impregnated Cu that is 0.058 cm³. The highest yield of ethanol as the product of glycerol degradation was 3.704% produced when the sonication times is 2 hours using activated natural zeolite catalyst. The activated zeolite has a prospect to be used as a degradation reaction catalyst for molecules that goes through the Bronsted Lowry acid mechanism.

Keywords: Catalysts, degradation of glycerol, ethanol production, mordenite, sonication

1. Introduction
Currently, new and renewable energy is an important issue according to the depletion of fossil fuels. The BPPT data in 2011 states that Indonesia's total oil reserves was 7.73 billion barrels and fell to 7.41 billion barrels in 2012 [1]. The rate of the consumption of petroleum increase along with the increase in population [2]. It is estimated that 15 to 20 years later the fossil energy source will run out. Considering that existing fossil material is limited and non-renewable resource, efforts should be made in the use of alternative energy considered technically, economically, and environmentally feasible [3,4]. This idea is in line with Presidential Instructions No.1 2006 on the supply and utilization of biofuel as an alternative fuel.

Biodiesel has become a renewable fuel that proves to be suitable as an alternative fuel for diesel engines. It is estimated that biodiesel can contribute as much as 20% to all transport fuels by 2020 [5]. The higher the production of biodiesel the higher the amount of glycerol as a by-product. Glycerol is obtained by the transesterification process of triglycerides/vegetable oils on biodiesel production [6,7]. A total of 1 mol of glycerol can be produced by every 3 moles of biodiesel production through transesterification reaction or about 10% of total weight [5]. The abundance of glycerol waste makes it have a low price of glycerol in the market, ranging from 1.28 to 1.50 US$ per kilogram [8]. The availability of glycerol that is inexpensive and has the potential to be utilized as a new type of energy that has high economic value like ethanol, methanol, acrolein, and allyl alcohol.
Buhler et al. [9] had conducted glycerol conversion through the glycerol molecular breaking reaction using aqueous media near the critical point. The reaction was run at a temperature of 622 to 748 K, pressures of 25, 35, and 45 MPa, the duration times of 32 to 165 seconds with varying concentrations. The products obtained were ethanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, methanol, formaldehyde, carbon monoxide, carbon dioxide and hydrogen. Meanwhile, Yuniati et al. [10] stated that glycerol could be converted to ethanol and methanol through the glycerol molecule breaking reaction. This process was carried out at 400 °C and the pressure of 250 bars. The highest yield obtained was ethanol of 1.3 %wt and methanol of 16.7 %wt. This process, however, is less feasible because it is done at high temperature and pressure. Corma et al. [11] explain that glycerol can be converted through a series of reactions including dehydration, cracking, hydrogen transfer, and catalyzed using HZSM-5 to produce acrolein. The study of converting glycerol using H-Zeolite size 200 mesh at 350-500 °C was also obtained acrolein [6].

The previous studies described that the components of glycerol are potential to be utilized in a new type of energy. However, the degradation of glycerol still requires enormous energy in the use of high temperature and pressure. It is necessary to find an alternative glycerol degradation technology that requires cheaper and safer operational costs.

The utilization of ultrasonic began to be used for macromolecular degradation [12]. The degradation of glycerol using γ-alumina catalyst with a sonication technology yielded the highest yield methanol of 6.297 %wt when it was conducted at 50 °C for 70 minutes, allyl alcohol of 5.503 %wt when it was conducted at 30 °C for 70 minutes, and acrolein of 18.878% when it was conducted at 30 °C for 30 minutes [13]. This research used an activated natural zeolite/Cu catalyst with various sonication times for converting glycerol to ethanol. The expected product, ethanol, is one of the most widely used of fuels.

2. Materials and Methods

2.1. Materials

The materials used in this research were natural zeolite from South of Malang East Java Indonesia, glycerol, oxalic acid, NaOH p.a., Cu (NO\textsubscript{3})\textsubscript{2}.3H\textsubscript{2}O p.a., an indicator of phenolphthalein, and demineralized water.

2.2. Methods

Natural zeolite was crushed and sieved into fine grains of 100 to 200 mesh. The zeolite was activated by calcination method at 500 °C for 5 hours. A part of the activated zeolite was impregnated with Cu so that the catalyst composes 15%wt of Cu. The impregnation was carried out using soaking the activated zeolite with a solution of Cu (NO\textsubscript{3})\textsubscript{2} then stirred using a shaker for 24 hours at the temperature of 60 to 70 °C. The impregnated of the activated zeolite then washed with demineralized water and dried at 110 °C for 24 hours. Both activated zeolites with or without impregnation were characterized using X-ray Diffraction (XRD) to determine the structure of zeolite and characterized using Brunauer-Emmett-Teller (BET) to determine the specific surface area and pore size. The degradation of glycerol to ethanol using a catalyst at the various time was assisted by ultrasonic of BRANSON 1510 at a frequency of 42 kHz. The products of glycerol degradation were analyzed using a Gas Chromatography (GC).

3. Results and Discussion

3.1. Calcination of natural zeolite

The aims of calcination is to release water molecules or hydrates attached to the pores or zeolite cavities. The loss of the water molecules can raise the cavity empty of the zeolite pores, so that expand the surface area of the zeolite. The physical change of zeolite because of calcination was a change in the zeolite color from gray to brown.
3.2. Characterization of Activated Natural Zeolite / Cu Using XRD

Impregnation was done by submersion activated natural zeolite into a solution of Cu(NO₃)₂ (aq). The impregnation of copper was expected that this metal can be dispersed evenly throughout the surface and the pores of the zeolite. The impregnated metal on the active site of the zeolite was considered to affect the character of the zeolite catalyst. The study of Bhatia et al. stated that with a more optimal dispersion of impregnated metal will increase the active site on the catalyst [14]. The structure of natural zeolite and natural zeolite-Cu were characterized using an XRD. The spectra generated from the XRD was analyzed and matched to the JCPDS (Joint Committee on Powder Diffraction Standards) data [15].

![Figure 1. Diffractogram Activated Natural Zeolite (ANZ) and Activated Natural Zeolite ANZ-Cu.](image)

The result of X-ray diffraction scanning on natural zeolite samples shows that the mineral was mordenite indicated by the emergence of peak region 2θ, while the level of component and crystallinity was indicated by the high peak intensity. Peaks pattern (Figure 1) shows that there is a similarity with peaks pattern of zeolite MOR according to JCPDS standard. In more detail can be seen in Table 1.

Based on the mapping of X-ray diffraction spectra between natural zeolite and JCPDS. There is a very high similarity in the appearance of the major peaks at the 2θ angle and also the intensity. The similarity of the diffractogram pattern of the main peaks in the same 2θ angles shows that the materials have the same structure [16,17]. Therefore it can be concluded that natural zeolite from Southern Malang is a Mordenite.

Meanwhile, XRD diffractogram of natural zeolite - Cu did not differ greatly with active natural zeolites as shown in Figure 1. The Diffractogram shows that zeolite impregnated of Cu only slightly change the number of peaks and its intensity compared to zeolite non-impregnated. The presence of Cu doped in the zeolite makes the crystallinity a slight increase. The impregnated Cu metal into the zeolite mostly forms CuO and Cu₂O, but there is also a small form of Cu. It can be seen in the diffractogram at 2θ emerging peaks around 44.3235°; 50.9708°; and 72.7535° which denotes the formation of Cu metal on zeolites corresponding to JCPDS Cu 04-0836. However, at the diffractogram also peak at 2θ around 35.6939°; 48.4564°; 60.7851° and 64.5100° which indicates CuO formed in the zeolite and peak 46.5855° which indicates the formation of Cu₂O in the zeolite.
Table 1. The data of main peaks at 2θ angles of Activated Natural Zeolite and zeolite MOR standard

| Activated Natural Zeolite | Zeolite MOR standard |
|---------------------------|----------------------|
| 2θ (°)  | d-spacing (Å) | 2θ (°)  | d-spacing (Å) |
| 13.4271 | 6.59454        | 13.45   | 6.584        |
| 15.2485 | 5.81067        | 15.30   | 5.791        |
| 19.5765 | 4.53472        | 19.61   | 4.527        |
| 21.3778 | 4.15653        | 21.45   | 4.142        |
| 22.2405 | 3.99722        | 22.20   | 4.004        |
| 23.3483 | 3.81001        | 23.64   | 3.764        |
| 25.6023 | 3.47946        | 25.63   | 3.476        |
| 26.2786 | 3.39165        | 26.25   | 3.395        |
| 27.6118 | 3.23063        | 27.67   | 3.223        |
| 30.8655 | 2.89709        | 30.89   | 2.894        |
| 35.6376 | 2.51934        | 35.61   | 2.521        |

3.3. Characterization of Activated Natural Zeolite/Cu Using BET

The analysis using the BET method was performed to find out the specific surface area and to know the pore volume of zeolite. There are two types of zeolites that are analyzed namely activated natural zeolite and activated natural zeolite impregnated Cu. The results of the BET analysis of activated natural zeolite and activated natural zeolite impregnated Cu are presented in Table 2.

Table 2. BET Analysis of Activated Natural Zeolite (ANZ) and Activated Natural Zeolite-Cu (ANZ-Cu)

| Type of Catalyst | Surface area (m²/g) | Total of Pore Volume (cm³/g) |
|------------------|---------------------|-------------------------------|
| ANZ              | 99.096              | 0.026                         |
| ANZ-Cu           | 6.597               | 0.058                         |

The results of the BET analysis shows that the ANZ had a surface area of 99.096 m²/g and a pore volume of 0.026 cm³/g. Meanwhile, ANZ-Cu had a surface area of 6.597 m²/g and a pore volume of 0.026 cm³/g. It means that the surface area of ANZ is higher than that of ANZ-Cu, but the pore volume of ANZ is smaller than that of ANZ-Cu. The surface area of these natural zeolites both ANZ and ANZ-Cu are smaller than that of synthetic zeolite, ie 374 m²/g [18]. It can be possible because the natural zeolite still contains impurities which cover some of its pores thereby lowering the surface area. The decreasing surface area of ANZ-Cu can be considered that Cu closes several pores of the catalyst. Furthermore, it can be denoted that activated natural zeolite non-impregnated of Cu has a good adsorption power.

3.4. Degradation of Glycerol becomes Ethanol.

The catalyst of ANZ or ANZ-Cu here serves to decrease the intra-molecular bonding force within the glycerol molecule, so it is easy to react with the H⁺ present in the mixture. The reaction can be seen in Figure 2.

3.5. Degradation Product as a function of the type of catalyst and sonication time

The product of degradation was analyzed using a Gas Chromatography. The analysis was proposed to find out qualitatively and quantitatively what the product is. The GC chromatogram data of the glycerol degradation products is shown in Table 3. The data showed that the product formed by the reaction of glycerol degradation is ethanol. The similar product was obtained on the degradation of glycerol that is ethanol through water supercritical conditions [19], using Ni/γ-Al2O3 Catalyst [9], [20]. However, Buhler et al. [9] state that ethanol is a product that occurs at high temperatures and through free radical mechanisms.
Figure 2. Mechanism of Glycerol Degradation Using a catalyst of ANZ or ANZ-Cu.

Based on the time variations performed on both catalysts, they showed that the highest yield of ethanol when it was conducted for 2 hours of sonication time with ANZ that is 3.704 %wt. The percentage of ethanol produced from the degradation of glycerol using ANZ catalyst was higher than that of using ANZ-Cu catalyst.

| Samples     | Time (minute) | Area (pA*s)   | Conc. EtOH (%wt) | Product |
|-------------|---------------|---------------|------------------|---------|
| ANZ- 1 hour | 0.962         | 1.54400e5     | 0.849            | EtOH    |
| ZA- 2 hours  | 0.953         | 6.73164e5     | 3.704            | EtOH    |
| ZA- 4 hours  | 0.955         | 1.92004e5     | 1.056            | EtOH    |
| ZA-Cu- 1 hour| 1.066         | 2.27243e4     | 0.125            | EtOH    |
| ZA-Cu- 2 hours| 0.997        | 1.02768e5     | 0.565            | EtOH    |
| ZA-Cu- 4 hours| 1.030        | 6.50366e4     | 0.358            | EtOH    |

According to sonication times, the highest yield of ethanol obtained when hydrolysis was conducted for 2 hours. The longer time of two hours sonication shows that the yield of ethanol produced was smaller. It can be stated that the optimal sonication time was 2 hours. At a longer time of sonication causes the ethanol to be degraded furthermore into smaller molecules. This product (ethanol) can be decomposed into CO, CO$_2$, and H$_2$ [20,21] so that the yield of ethanol becomes smaller at a longer time of sonication.

4. Conclusion
The structure of natural zeolite catalyst is a mordenite. The activated natural zeolite has the surface area of 99.096 m$^2$/g larger than that of activated natural zeolite-Cu that has a surface area of 6.597 m$^2$/g. However, the total pore volume activated natural zeolite of 0.026 cm$^3$/g is smaller than that of activated natural zeolite active-Cu of 0.058 cm$^3$/g. Both catalysts, ANZ and ANZ-Cu, provide a glycerol degradation to produce ethanol. The metal of Cu impregnated to zeolite catalyst decreases the yield production of ethanol. The optimum sonication time for glycerol degradation using both catalysts of ANZ and ANZ-Cu is 2 hours.

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