Conversion of Bioethanol to Diethyl Ether Catalyzed by Sulfuric Acid and Zeolite

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Abstract

Ethoxy ethane, or diethyl ether, has been successfully synthesized through the condensation reaction of bioethanol produced from fruit waste fermentation using acid-activated H-Zeolite, H2SO4/H-Zeolite, and H2SO4 as catalysts. Zeolite activation was carried out using the acidification method with 1 M, 2 M, 4 M, and 6 M H2SO4 for 24 hours. Activated zeolites were characterized using infrared spectroscopy, X-ray diffraction, and NaOH titration. The condensation reaction of bioethanol was carried out by catalysis of H2SO4/H-Zeolite with various concentrations of 1 M, 2 M, 4 M, and 6 M and catalyzed by 2 M, 4 M, and 6 M acid-activated H-Zeolite. The condensation reaction process was carried out with a ratio of bioethanol to catalyst of 2:1 (w/w) using the fractional distillation method. Ethoxy ethane resulting from the condensation reaction was characterized using a GC instrument.

The results showed that zeolite activation using 2 M, 4 M, and 6 M H2SO4 increased the crystallinity and the acidity of natural zeolite from 1.50 mmol/gram to 2.50 mmol/gram. The optimum ethoxy ethane was obtained through the use of 2 M H2SO4/H-Zeolite and 2 M H2SO4-activated H-Zeolite as catalysts, yielding 23.72% and 22.43%, respectively. H2SO4/H-Zeolite homogeneous catalyst could produce ethoxy ethane in a greater amount than H-Zeolite catalyst.

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Introduction

Most people only use fruit waste to obtain biogas and dispose of the solid and liquid forms of it. In fact, solid waste that comes from fruit contains a lot of cellulose and glucose, which can actually be utilized after converted to be ethanol [1-3]. The fermented ethanol can then be used as a raw material in the process of making ethoxy ethane, which has higher economic value.

Ethoxy ethane is a compound that can be used as a booster for cetane numbers in diesel fuel [4]. Types of ether that are often used as a booster for octane numbers include Methyl Tertiary-Butyl Ether (MTBE) and Ethyl Tertiary-Butyl Ether (ETBE). In recent periods, ethoxy ethane compounds have begun to be used as boosters of cetane numbers in diesel or biodiesel engines, because they have high cetane numbers [5]. The ethoxy ethane conversion produced using the Barbet method can reach 90-94%. However, the catalyst used is a homogeneous catalyst that is liquid and corrosive, so the catalyst separation process is still difficult and expensive. Therefore, several heterogeneous catalysts that are non-corrosive and easy to separate have been developed. Heterogeneous catalysts that have been successfully developed for the ethanol condensation process include silica-alumina, MgO, alumina, and WO3. Golay et al. (1999) have conducted research using an alumina catalyst which has been modified by Mg2+ ions to condense ethanol [6], while Haber et al. (2002) used a potassium salt catalyst derived from tungstophosphoric acid (HFW), which has the formulation of KxH3-xPW12O40 and AgxH3PW12O40 [7]. Further research was carried out by Zaki (2005) using a catalyst mixture of metal oxides containing iron and manganese oxides with alumina and or without silica gel [8]. However, from some of these studies, the catalyst used is still using a metal mixture which has a high level of difficulty in its manufacture. Besides, the metals used in the process of making catalysts are limited in number and the prices are relatively expensive. The temperature used in the catalyst-making process is relatively high so that it is economically insufficient. Therefore, this research proposed a catalyst from natural zeolites, whose abundance and purity are quite high in Indonesia.

This research was conducted by utilizing raw materials derived from fruit waste as the main raw material obtained from the Gamping Fruit Market, which has a fairly large level of waste production, namely 4 tons per day. Also, this study studied the possibility of using heterogeneous catalyst H-zeolite to reduce the amount of $\text{H}_2\text{SO}_4$ used in the condensation process from bioethanol to ethoxy ethane.

Experimental Section

Materials

The main materials used included fruit waste obtained from Gamping Fruit Market, yeast, p.a ethanol (E. Merck), technical diethyl ether, filter paper, natural zeolite, $\text{H}_2\text{SO}_4$ (E. Merck), and universal pH indicators. Supporting materials used were distilled water, aquabides, NaOH (E. Merck), CaCO3 (E. Merck), AgNO3 solution, aluminum foil paper, as well as solid CO2 and phenolphthalein indicators.

Equipments

The equipments used in this study were laboratory glassware, fermentation vats, a set of distillation-fractionation tools, chopper, pounder, bath, 250 mesh sieve, oven, porcelain exchange, a set of titration tools, alcohol meter, analyte weighing device (Metlller- AT 200), infrared spectroscopy type FTIR 8201 PC Shimadzu (Department of Chemistry, Faculty of Mathematics and Natural Sciences UGM), X-ray Diffraction “Perkin Elmer 3110” type XRD 6000 X Shimadzu (Department of Chemistry, UGM), Gas Chromatography “Hewlett Packard 5890 series II” (GC), a centrifuge (Kokusan Ogawa Seiki Co. Ltd).

Bioethanol manufacturing

A total of 10 kg of chopped fruit waste was put in a fermenting container and added with yeast as much as 5% (w/w) of the fruit waste. The fermentation was left for 72 hours in the fermenting container and stirred periodically. The liquid product obtained was collected and filtered and then distilled. The distillate was then analyzed using GC.

Heterogeneous catalyst (H-Zeolite) preparation

The washed 250 mesh zeolites, each weighing 60 grams, were immersed in 100 mL $\text{H}_2\text{SO}_4$ with concentrations of 1, 2, 4, and 6 M and stirred for 24 hours. The mixture was then washed using distilled water until free of sulfate ions (until showing a negative test for AgNO3). The sulfated zeolite was dried at a temperature of 100-120°C and then crushed and sieved using a 250 mesh sieve.
Zeolite acidity test

The zeolite acidity test in this study was determined using the titration method. The titration test was carried out using NaOH. The titration test was intended to determine the number of protons (H⁺) in the H-Zeolite. The titration test was carried out by dispersing 0.5 grams of 1 M H-Zeolite in 15 mL of 1 M NaOH and stirring for 15 minutes, and then adding 3 drops of PP indicator and, subsequently, titrating using 1 M H₂SO₄.

Ethanol condensation

The mixture of bioethanol and H-Zeolite catalyst were made with a variety of catalysts (weight ratio of bioethanol:catalyst = 2:1). The mixtures were stirred while heating at 140-160 °C for 8 hours for each variation of catalyst and bioethanol. The results of the distillate were collected into a container in the form of a bottle and analyzed using GC.

Results and Discussion

Zeolite acidity

Titration aims to determine the number of protons (H⁺) contained in H-Zeolite as a catalyst. The acidity of the zeolite can come from the Lewis acid site, namely from Al, as well as from the Brönsted acid site, namely H⁺. A zeolite which has a greater amount of Al in their skeleton will have a large Lewis acid site. Likewise, a zeolite which has a large amount of H⁺ will have a large Brönsted acid site. Vieira et al. has illustrated the sulfation process of zeolites in their research on the effect of calcination temperature on catalysis and the acidity of zeolite group materials for biofuel production (Figure 1).

Figure 1. Illustration of the sulfation process in zeolites [9].

The following Table 1 shows that the addition of H₂SO₄ with various concentrations including 1 M, 2 M, 4 M, and 6 M into the zeolite cavity can increase the acidity of the zeolite. H-Zeolite was dispersed into NaOH to react the H⁺ in the catalyst with NaOH, the excess base was then titrated with sulphuric acid and determine the volume of NaOH reacted with H⁺ in catalyst by subtracting the initial NaOH with the excess base. The amount of NaOH reacted with the protons contained in a zeolite corresponds to the acidity of the zeolite.

Table 1. Zeolite acidity, based on the titration test with NaOH.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[NaOH] (M)</th>
<th>V_{NaOH} (mL)</th>
<th>Acidity (mmol/gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Zeolite</td>
<td>1 M</td>
<td>30</td>
<td>1.50</td>
</tr>
<tr>
<td>1 M H-Zeolite</td>
<td>1 M</td>
<td>4</td>
<td>0.13</td>
</tr>
<tr>
<td>2 M H-Zeolite</td>
<td>2 M</td>
<td>14</td>
<td>0.15</td>
</tr>
<tr>
<td>4 M H-Zeolite</td>
<td>4 M</td>
<td>10</td>
<td>3.60</td>
</tr>
<tr>
<td>6 M H-Zeolite</td>
<td>6 M</td>
<td>18</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Synthesis and Characterization of fruit waste-based ethanol

From the result of GC analysis (Figure 2), it was found that the ethanol peak appeared at the retention time of 3.081 minutes with the percent (%) area of 75.31%. The bioethanol produced was then distilled to obtain bioethanol with a concentration of 80% as a precursor in the manufacture of sulfuric acid and H-Zeolite-catalyzed ethoxy ethane.

Figure 2. Ethanol chromatogram from fruit waste obtained from Gamping Fruit Market.

Synthesis and characterization of H-Zeolite

Figure 3 shows that compared to natural zeolite, acidified zeolite does not change the mineral content and does not damage the zeolite structure by the increase in the concentration of acid used in the immersion process. This is indicated by the absence of a peak shift in the infrared spectra band. The area of wavenumber 3600 cm⁻¹ is the peak for –OH alumino al, the area of wavenumber 3400 cm⁻¹ is the peak for –OH silanol, while the area of wavenumber 1600 cm⁻¹ is the peak for bending –OH in water [10]. The area of wavenumber 1000 cm⁻¹ is the absorption peak indicating SiO stretching, while the area of the wavenumber 470 cm⁻¹ is the absorption peak indicating symmetrical stretching vibration between the TO₄ tetrahedra which is an external vibration.
XRD results (Figure 4) showed that the immersion process using acid (H\(_2\)SO\(_4\)) did not change the mineral content and did not damage the zeolite structure. This is indicated by the absence of peak shifts and peak widening in the XRD results. The relative amount of zeolite before and after acid activation can be determined by comparing the intensity of natural zeolite with acid-activated zeolite (1 M H-Zeolite and 6 M H-Zeolite'). XRD results also showed that the zeolite activation process using acid caused an increase in the relative amount of mordenite and clinoptilolite [11].

H-Zeolite, H\(_2\)SO\(_4\)/H-Zeolite and H\(_2\)SO\(_4\)-catalyzed bioethanol condensation

Fermented bioethanol was converted into ether compounds through a condensation process catalyzed by H\(_2\)SO\(_4\) and H-Zeolite with various variations (1, 2, 4, and 6 M) and H-Zeolite with the same variations. The results of each catalysis product were characterized using GC. The chromatogram of the condensation products, namely ethanol and ethoxy ethane, is shown in Figure 5, which shows the decrease in ethoxy ethane concentration with the increase in the amount of sulfuric acid added into zeolite. The increasing acidity of the catalyst affected the product resulted.
Table 2 shows the tendency that the greater the acid used as a catalyst in the condensation process of H₂SO₄ and H-Zeolite catalyzed bioethanol, the lower concentration (%) produced.

Table 2. Ethoxy ethane resulted from the condensation reaction of bioethanol catalyzed by H₂SO₄ and H-Zeolite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Product</th>
<th>Ethoxy ethane (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioethanol : H₂SO₄ + 1 M</td>
<td>Ethanol</td>
<td>0</td>
</tr>
<tr>
<td>H-Zeolite catalyst</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bioethanol : H₂SO₄ + 2 M</td>
<td>Ether</td>
<td>23.72</td>
</tr>
<tr>
<td>H-Zeolite catalyst</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bioethanol : H₂SO₄ + 4 M</td>
<td>Ether</td>
<td>23.68</td>
</tr>
<tr>
<td>H-Zeolite catalyst</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bioethanol : H₂SO₄ + 6 M</td>
<td>Ether</td>
<td>23.53</td>
</tr>
<tr>
<td>H-Zeolite catalyst</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Meanwhile, the data in Table 3 also shows a tendency that the greater the concentration of acid used as a catalyst, the lower the concentration (%) of the ether compound produced. As also seen in Figure 6, in the bioethanol condensation process catalyzed by the solid acid H-Zeolite, the greater the acid concentration of H-Zeolite, the lower concentration (%) resulting from the condensation process because the Brönsted acid site of the H-Zeolite catalyst contained in the pore can be optimally immobilized. In the zeolite framework which consists of a TO₄ (T = Si or Al) bond, the Si-O bond is much stronger than the Al-O bond. Atoms of Si (group IV A in the Periodic Table of the Elements) which have a smaller radius than Al when they are bonded to O atoms, their bonds tend to be polarized so that the bond distance will be closer, which means that the bond strength will also increase. A strong bond has high thermal stability. One of the conditions for good material to be used as a catalyst is that it has high thermal stability.

Table 3. Ethoxy ethane resulted from the condensation reaction of bioethanol catalyzed by H-Zeolite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ethoxy ethane concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioethanol : H-Zeolite 2 M</td>
<td>22.43</td>
</tr>
<tr>
<td>Bioethanol : H-Zeolite 4 M</td>
<td>22.22</td>
</tr>
<tr>
<td>Bioethanol : H-Zeolite 6 M</td>
<td>22.21</td>
</tr>
</tbody>
</table>

The more H₂SO₄ acid used when immersing the zeolite can remove the amount of Al that is owned by the zeolite so that the zeolite tends to be positively charged. Thus, the proton (H⁺) in H₂SO₄ that should be able to bind and attach to the oxygen atom around the Al atom does not occur, resulting in a reduced Brönsted acid site on the zeolite [12].

![Figure 6. Chromatogram of the condensation of bioethanol catalyzed by solid acids (a) 2 M H-Zeolite, (b) 4 M H-Zeolite, and (c) 6 M H-Zeolite.](image)
ethoxy ethane with concentration (%) up to 90%. In this study, the Barbet process was also carried out, namely the production of ethoxy ethane using a sulfuric acid (H₂SO₄) catalyst. Figure 7 shows higher concentration of ethoxy ethane resulted from H₂SO₄-catalyzed condensation reaction.

**Figure 7.** Chromatogram of the condensation of bioethanol catalyzed by H₂SO₄.

It can be seen from Figure 8 that the chemical shift area δ = 1.2 ppm is the chemical shift for the methyl group. The methyl group appears in the chemical shift region closest to the TMS because it is the least protected. The further a group (structurally) from the TMS, the easier the group will be read by the detector. The peak in the chemical shift region δ = 3.8 ppm is the shift from the methylene group (-CH₂). The peak of the methylene group (-CH₂) appears after the methyl peak (-CH₃) because of its position before the methyl group (-CH₃) so it is more protected when compared to methyl (-CH₃). Thus, from the results of the ¹H-NMR spectrum, it can be concluded that the product resulting from the condensation reaction of bioethanol is an ethoxy ethane compound with the molecular formula C₄H₁₀O.

**Figure 8.** ¹H-NMR spectra of ethoxy ethane resulted from H₂SO₄-catalyzed condensation reaction.

From the characterization of the resulting condensation, it appears that ethoxy ethane products are produced in the catalysis process using both H₂SO₄ and H₂SO₄/H-Zeolite, compared to catalysis with H-Zeolite alone. This can be due to the fact that H-Zeolite is a weaker acid, compared to sulfuric acid (H₂SO₄), and has a different phase in the dispersing system so that the contact that occurs between ethanol and catalyst is possible only on the surface of the H-Zeolite and the surface or at the mouth of the pore of H-Zeolite only. As a result, not all of the Brønsted acid sites on H-Zeolite can be utilized optimally. This is what is thought to cause H₂SO₄ in the condensation reaction of bioethanol to produce higher concentration (%) of ethoxy ethane when compared to heterogeneous catalysts: H-Zeolite, and even H₂SO₄ and H-Zeolit. Therefore, the presence of H₂SO₄ in the catalyst has advantages when compared to the H-Zeolite catalyst.

**Conclusion**

Zeoites, after being activated using H₂SO₄ with various concentrations, have catalytic properties that can be used in bioethanol condensation reactions. H-Zeolite as a heterogeneous catalyst produces a lower amount of product than H₂SO₄/H-Zeolite and H₂SO₄ catalysts. From the research conducted, it was obtained that the optimum results of ethoxy ethane were obtained through the use of H₂SO₄/2 M H-Zeolite catalyst and H₂SO₄-activated 2 M H-Zeolite yielding 23.72% and 22.43%, respectively.

**Conflict of interest**

The authors declare no conflict of interest in this study.

**References**


