Characterization and Utilization of Gunungkidul Natural Zeolite for Bioethanol Dehydration

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\textbf{Abstract}

Bioethanol purification process after the fermentation process was done in two stages, namely distillation and dehydration. The dehydration can be carried out with molecular sieves, one of them by using natural zeolite. Therefore, the activity tests and characterization of Gunungkidul natural zeolites and commercial zeolite (import) were conducted. It was observed that the vapor phase dehydration using modified Gunungkidul natural zeolite has the ability to purify ethanol relatively similar to the commercial zeolite (purity more than 99\%) but has lower yield. Relatively much ethanol was absorbed by natural zeolite, as evidenced by the addition of adsorbent weight more than 20\%.

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Selection and peer-review under responsibility of the Scientific Committee of Indonesia EBTKE Conex 2013

\textbf{Keywords:} bioethanol, purification, dehydration, commercial zeolite, Gunungkidul natural zeolite

\textbf{1. Introduction}

Indonesian natural zeolite deposits are large and have high purity with its silica concentration approximately 60\%. Several zeolite mines areas are South Lampung, Bayah, Cikembar, Cipatujah, Nangapada-West Java, Ende-

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Zeolite is a natural resource which is useful for the chemical industry in Indonesia. The first zeolite was discovered by Baron Axel Frederick C in 1756 at the nature for the hollow structure of type crystals. Zeolite was formed at various places in the earth, as well as on the sea bottom [2]. Zeolite is an inorganic polymer, which is composed of the smallest repeating units form of tetrahedral SiO₄ and AlO₄ [1]. Zeolites are aluminosilicates crystalline of group IA and IIA elements such as Na, K, Mg and Ca. It can be stated by empirical formula M₂/n Al₂O₃. y (SiO₂). wH₂O with “y” equal with 2 or greater, “n” is the valence of M cation and “w” equals the number of water molecules which contained in the pores of the zeolite [3].

Zeolites are the best adsorber for the adsorption process [4]. The utilization of zeolite as adsorber is due to its porous structure, molecular sieve and absorbing ability for small molecules such as water which can enter the zeolite [5]. There are about 40 types of natural zeolite, although about 12 types which has commercial value, including clinoptilolite, mordenit, filipsit, kbasit and erionite [1]. One of the natural zeolite deposits in Indonesia, which has a fairly large in amount with silica content of approximately 60% is the local zeolite of Gunungkidul – Yogyakarta with the deposit of 55,000,000 m³. These minerals are often found in the hills area of Baturagung, the District Gedangsari (Hargomulyo Village, Watugajah, Mertelu, and Tegalrejo) and Ngawen District (Tancep Village) [6].

Optimization of the natural zeolite performance needs to be done the activation stage before used as an adsorbent. Natural zeolite can be activated by heating (calcination) to evaporate the trapped water in the pores of zeolite crystals, so the surface area was increases [7]. Zeolites can be also activated through dealumination process by using acid to produce Wonosari (Gunungkidul) natural zeolite which was able to increase the surface area and pore volume, reducing the mean pore spokes, improving the ratio of Si/Al and acidity of natural zeolite [8]. After dealumination and calcination, natural zeolite Gunungkidul better than the previous process with higher SiO₂/Al₂O₃ ratio approaching that expected [1].

Natural zeolites have the framework structure, containing blank spaces which occupied by cations and free water molecules to allow the exchange of ions and absorption of chemical compounds [2]. Zeolite structure can perform adsorption and absorption of the compound H₂O, CO₂, SO₂, H₂S [9], with the gases absorption ability of zeolite is up to 25% [7]. Zeolites have the ability to increase the purity of biogas because it can absorb all the main impurity gases of water vapor (H₂O), CO₂ and H₂S [10]. Natural zeolites have the power to absorbs more water from the air than on silica gel [2]. Therefore, the activated natural zeolite can be used as an adsorbent for water in ethanol 95-96% which called bioethanol dehydration. The purpose of this research was to characterize and utilize Gunungkidul natural zeolite for bioethanol dehydration.

2. Material and method

2.1. Zeolite characterization

Natural zeolite, modified natural zeolite and commercial zeolite (import from foreign country) were characterized on crystallinity by Maxima Shimadzu XRD (X-Ray Diffraction) and specific surface area by Sorptomatic 1800 Carlo Erba Instruments.

2.2. Zeolite pre-treatment

Gunungkidul natural zeolites were crushed to 100 mesh size, dealuminated with HCl for 24 hours, formed pellets and calcined at 400 °C for 4 hours. Commercial zeolite was stored in oven with temperature of 105 °C in order to remain anhydrous.

2.3. Dehydrated trial using zeolite

Dehydration of ethanol was conducted on dehydration column with a length of 30 cm and a diameter of 2 inches. 96% ethanol dehydrated in the vapor phase current through the column which has been filled with zeolite. Dehydrated ethanol results levels was measured by using alcoholmeter.
3. Result and discussion

Characterization of crystallinity and specific surface area has been done for three type of zeolite which will be tested for bioethanol dehydration. They are natural zeolite, modified natural zeolite and commercial zeolite which shown on Figure 1.

![Fig. 1. Zeolite sample for characterization : (a) natural zeolite; (b) modified natural zeolite; (c) commercial zeolite.](image)

Figure 2 shows the significant crystallinity changes of the natural zeolite before and after modification. Chemical and physical treatments have been successful in impurities reduction and crystallinity improvement of the natural zeolite. XRD pattern of natural zeolite was also compared with commercial zeolite. Commercial zeolite showed higher crystallinity than the local natural zeolite.

![Fig. 2. Zeolite XRD patterns of natural zeolite (blue); modified natural zeolite (red); commercial zeolite (green).](image)

Characterization of specific surface area was done by using BET method as shown in Table 1. Zeolite samples having high surface area will have greater ability in adsorption. Large surface area allows to better contact between reactants and adsorbent, so that the reaction can be run more effectively. Specific surface area of the local natural zeolite zeolite is not much different from commercial zeolite. It indicated that there is similar adsorption ability between local natural zeolite and commercial zeolite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural zeolite</td>
<td>6.0632</td>
</tr>
<tr>
<td>Modified natural zeolite</td>
<td>4.1114</td>
</tr>
<tr>
<td>Commercial zeolite</td>
<td>6.9196</td>
</tr>
</tbody>
</table>
In comparative characterization of crystallinity and specific surface area, natural zeolite Gunungkidul has relatively close results with commercial zeolite, but has not been able to surpass or even. It still needs to be pursued reoptimization of the natural zeolite modification.

Vapor phase dehydration has been done by using modified natural zeolite Gunungkidul and commercial zeolite. It conducted on vertical dehydration column showed in Figure 3. The comparison results of bioethanol dehydration can be seen in Table 2.

Table 2 shows that the vapor phase dehydration using local modified natural zeolite was relatively successful (purity increases or more than 99%), but the dehydration yield is still low. This is possible because there are many ethanol absorbed by zeolite adsorbents which evidenced by zeolite weight gain more than 20%.

<table>
<thead>
<tr>
<th>Zeolite Type</th>
<th>Volume (ml)</th>
<th>Yield (%)</th>
<th>Zeolite Weight (g)</th>
<th>Increase Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>Commercial Zeolite</td>
<td>500</td>
<td>420</td>
<td>84</td>
<td>500</td>
</tr>
<tr>
<td>Modified Natural Zeolite</td>
<td>500</td>
<td>320</td>
<td>64</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>294</td>
<td>58.8</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>312</td>
<td>62.4</td>
<td>500</td>
</tr>
</tbody>
</table>

4. Conclusion

Vapor phase dehydration using modified natural zeolite Gunungkidul has been able to purify ethanol relatively same as with commercial zeolite (purity more than 99%), but lower in the yield.

Acknowledgements

The authors are thankful to UPT BPPTK LIPI Yogyakarta especially for Alternative Energy Team, Chemical and Environmental Technology Team for support of facilities in this research. Also, thankful to P2K LIPI especially for PN 8 : Bioethanol Lignocellulose Team.
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