Ethanol Purification Using Active Natural Pahae Zeolite By Adsorption Distillation Method

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Ethanol Purification Using Active Natural Pahae Zeolite By Adsorption Distillation Method

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Abstract. A research of ethanol purification using Natural Pahae Zeolite as active material has been carried. This research aims to analyze the process of ethanol purification by using adsorption distillation method followed analyze by the influences of the variants of its variables. Natural Pahae Zeolite which has been chemically activated by H2SO4 6% and physically by the variants of calcining temperatures at 500°C, 600°C, 700°C, 800°C and 900 °C. Then, continued by applying an adsorbent in the ethanol purification with the various time in 30 minutes, 45 minutes, 60 minutes, 75 minutes, and 90 minutes. The final ethanol which has been purified then analyzed by using Gas Chromatography (GC) to classify the level of its purity. From the result of the research, the most effective process in ethanol purification was the process of adsorption distillation by using natural pahae zeolite as the adsorbent which has been activated at 700°C in 60 minutes and heated at 78°C which resulted ethanol as 93.28%.

1. Introduction
Nowadays, the growth of industries and transportation come out with the growth of fuel oil consuming. It causes the decrease of fuel oil stock. The prediction of the decrease of fuel oil stock in the future and a bigger dependency of the fuel oil energy resource, make many scientists go on researches to find out and develop the alternate energy resource from renewable natural resources.

Not only that, the issue of global warming comes out from the increment of fuel oil consuming. The gas of the fuel which freed to atmospheres has caused a significant environment issue such global warming [1]. The using of ethanol as a fuel will decrease the pollution which caused by the emission of fuel oil in the environment [2]. Ethanol is one of alternate energy resource which is prospective to be developed in Indonesia as a substitution or additives fossil fuel which has been using now, such as gasoline. It is because ethanol's material comes from Indonesia which is renewable and environmentally freindly. But the using of ethanol as a fuel isn’t a solution because it costs a lot. The minimum production of ethanol and a high production fee make ethanol limited and costs more.
Pertamina Persero even has to stopped the ethanol production because those kinds of factors. So, now there are some researches which aim to press the ethanol cost by using the cheap provides material and certainly will produce a high level of ethanol.

Many researches has used zeolite as the adsorbent on the bioethanol purification. Novitasari reported [2] the purification of bioethanol using adsorption process and adsorption distillation in 50 minutes and at 78°C. In the other hand, by using zeolite as adsorbent which has been activated in 300 °C could increase the purity of bioethanol from 80% to 98.42%.

Khaidir reported [3] the dehydration of ethanol by using natural zeolite which has been modified could level up 1.38% for 90% bioethanol and level up 1.27% for 95% bioethanol. The research using the aluminate method such as oxide aluminium, nitrate aluminium, alum and kaolin as the zeolite preparation. Dehydration was done by distillation method in 30 minutes and heated in 75 °C.

The using of natural zeolite as the water adsorbent in the purification process basically from the nature of zeolite itself which is as adsorbent, and the other supporting factor is the limitless of zeolite in Indonesia, low costs, and many relate supported researches which have been done before. In the research, the natural zeolite which use are taken from sub-district Pahae, distict of North Tapanuli.

2. Materials And Method Of Research

2.1 Materials
Materials which were used natural Pahae zeolite which was taken from North Tapanuli, H₂SO₄ 6%, Ethanol PA 99.8%, Ethanol 90%, filter paper, and destilled water.

2.2 Tools
Tools which were used in the research adalah Energy Dispersive X-ray Spectrometer (EDX), Gas Chromatography (GC), strainer 200 mesh, furnace, oven, analytic scale, beaker glass in various size, measuring cup, spatula, bunche coneo mortar, magnetic stirer, and another set of adsorption distillation tools as the figure follows.

![Figure 1. Adsorption Distillation Tools Series](image)

2.3 Procedure
There were two steps in the process of ethanol purification. First of all was the preparation of zeolite as the adsorbent. First crushing the chunck of natural zeolite into powder which size is 200 mesh, then soaked into H₂SO₄ 6% for 3 hours then stir using stirer, then zeolite was washed by destilled water until reach the neutral pH. Next, zeolite was dried by heating in an oven at 110°C for an hour. After that, the dried zeolite was calcinated at 500 °C to 900 °C for 3 hours. After that zeolite is ready to be used. In this step, we need to do a characterization test on the ability of water adsorption, and identification on the unsure to define whether the natural pahae zeolite which has been activated suitable to be used as water adsorbent in the ethanol purification by using adsorption distillation
method. The second step was the application of zeolite as the adsorbent. Zeolite and ethanol were put into the filling materials column then stirred based on certain variable of time. Then, adsorption distillation was done at temperature 78 °C constantly.

3. Result And Discussion
The results will be discussed in 3 subsections, they are water adsorption ability, unsure identification, and purification test result

3.1. Water Adsorption Ability
The result of nonactivated natural zeolite water adsorption ability, natural zeolite activated physically and natural zeolite activated physically-chemically in calcining at 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C were shown in Figure 2.

![Graph of Relation Between Adsorption ability with Temperature](image)

**Figure 2. Graph of Relation Between Adsorption ability with Temperature**

In Figure 2, the highest percentage of water adsorption was shown by natural zeolite which has been activated physical-chemically activated 53.82% in calcining at 700 °C, meanwhile the lowest percentage of water adsorption was shown by natural zeolite which has been activated only physically at 900 °C. Nonactivated zeolite has the lowest water adsorption ability because the pores of zeolite have not fully formed and there was still dirt or another useless particles on the pores surface. Zeolite Activated has more ability compared to zeolite which has been not activated because the pores has fully formed. eventhough there was still dirt or another particles on the pores surface. Zeolite that has been physical-chemically activated has the highest absorption if compared by the zeolite was not activated and activated zeolite only physically due to the zeolite pores already fully formed and no
3.2. Unsure Identification

Energy Dispersive analysis of X-ray Spectrometer (EDX) nonactivated natural zeolite particles and activated natural zeolite physical and chemically is intended to know the elements that are contained in the particles of natural zeolite through the graph of the relationship between our two elements (V) against the intensity count per second (cps) which means the greater the intensity of that appears, the more the content elements in a substance. Figure 3 and 4 present the results of tests EDX data on physics activation zeolite-chemical and nonactivated.

**Figure 3. The Results of Tests EDX on Physical-Chemically Activated Zeolite**

<table>
<thead>
<tr>
<th>Element</th>
<th>Series</th>
<th>C norm. C Atom. C Error</th>
<th>[wt.%]</th>
<th>[at.%]</th>
<th>[at.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>K-series</td>
<td>25.68</td>
<td>35.34</td>
<td>8.21</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>K-series</td>
<td>41.23</td>
<td>49.91</td>
<td>6.77</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>K-series</td>
<td>0.73</td>
<td>8.45</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>K-series</td>
<td>0.51</td>
<td>0.36</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>K-series</td>
<td>5.42</td>
<td>3.13</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>K-series</td>
<td>18.16</td>
<td>9.25</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>K-series</td>
<td>2.51</td>
<td>0.92</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>K-series</td>
<td>1.31</td>
<td>0.46</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>K-series</td>
<td>1.07</td>
<td>0.27</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

*Total: 115.59 100.00 100.00*

**Figure 4. The Results of Tests EDX on Non-Activated Zeolite**

<table>
<thead>
<tr>
<th>Element</th>
<th>Series</th>
<th>C norm. C Atom. C Error</th>
<th>[wt.%]</th>
<th>[at.%]</th>
<th>[at.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>K-series</td>
<td>16.35</td>
<td>24.37</td>
<td>2.62</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>K-series</td>
<td>49.98</td>
<td>55.94</td>
<td>6.06</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>K-series</td>
<td>0.72</td>
<td>0.56</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>K-series</td>
<td>0.41</td>
<td>0.30</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>K-series</td>
<td>6.27</td>
<td>4.16</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>K-series</td>
<td>19.40</td>
<td>12.37</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>K-series</td>
<td>2.76</td>
<td>1.26</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>K-series</td>
<td>1.06</td>
<td>0.47</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>K-series</td>
<td>0.29</td>
<td>0.11</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>K-series</td>
<td>1.13</td>
<td>0.36</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>K-series</td>
<td>0.33</td>
<td>0.09</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>

*Total: 98.69 100.00 100.00*
Zeolite contains the main elements, aluminum, silicon and oxygen and bind a certain water molecules in its pore. Other elements are also found in the zeolite are the element of the alkali metal and ground alkali. This is supported from the results of the EDX analysis of natural zeolite particles activation results which are shown in Figure 3 which is known the dominant elements found on natural zeolite particles activation results were O (Oxygen) of 48.31 %, C (carbon) of 25.68 %, Si (Silica) of 15.71 %, Al (Aluminum) of 5.17%, while the other elements were impurity (dirt concentrate grade element).

Figure 4 shows the dominant elements that are located in the zeolite nonactivated were elements of O (Oxygen) of 50.64 %, C (carbon) of 16.57 %, Si (Silica) of 19.65 %, Al (Aluminum) of 6.35%, while the other elements were impurity (dirt concentrate grade element). From the picture is also seen that the natural zeolite before and after the activation is still contain substances - organic substances (the existence of atoms C) that would affect the ability of the zeolite adsorption against water vapor.

From the analysis result of EDX on Figure 3 and 4, the ratio of Si/Al nonactivated zeolite is 3.09 and the ratio of Si/Al activated zeolite is 3.03. It can be concluded that the activation on the zeolite affects the ratio Si/Al even though the value is not significant. But the results of composition analysis with EDX is generally still give the percentage of error so to provide more accurate analysis of composition it is recommended to use the atomic absorption spectrophotometer (ASA) [5].

Some types of zeolite based on the ratio of Si/Al, zeolite filter silica with ratio of Si/Al 1 - 1.5, it has a high concentration of the most abundant cation and have the nature of optimum adsorption, the examples of low silica zeolite is zeolite A and X; silica zeolite medium, which has a comparison of Si/Al is 2 -5, examples of this type of zeolite is Mordenite zeolite; high silica, with the comparison of the level of Si/Al between 10 - 100, even more, such as is ZSM -5 [6].

The ratio which obtained from the EDX analysis results show that the natural pahae zeolite is classified in silica medium zeolite such as Mordenite type. Type of Mordenite zeolite is the ability of adsorbing much H2O so natural pahae zeolite suitable to be applied as adsorbent of H2O in a mixture of ethanol-water.

3.3. Purification Test Result

The testing of zeolite as an adsorbent has done by using adsorption distillation method, it is a method of separation of two mixtures of liquid substance based on the difference of boiling point that includes the adsorption of dissolved substances [7].

The purities of ethanol adsorption distillation results follow AOAC method 2003 [8] (Association of Official Analytical Chemist) is tested by using Gas Chromatography stated in percent (%). The measurement of the indicator using Ethanol Absolute with purities 99.8 %. Purities were obtained by determining the comparison peak ethanol area that has been analyzed with the peak area of the ethanol times with the percentage of the indicators.

It has been obtained zeolite which has the highest water adsorption ability the zeolite which has been activated physical-chemically at a temperature calcining 700 °C, zeolite was then used for the process of adsorption distillation with contact time variations 30 minutes, 45 minutes, 60 minutes, 75 minutes and 90 minutes. The increase in the level of ethanol can be seen in the Table 1.

<table>
<thead>
<tr>
<th>No</th>
<th>Contact Time (minute)</th>
<th>Ethanol Level Before (%)</th>
<th>Ethanol Level After (%)</th>
<th>Percentage of Ethanol Increaseement Level (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>90</td>
<td>91,04</td>
<td>1,16</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>90</td>
<td>91,86</td>
<td>2,07</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>90</td>
<td>93,28</td>
<td>3,64</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>90</td>
<td>92,11</td>
<td>2,34</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>90</td>
<td>90,19</td>
<td>0,21</td>
</tr>
</tbody>
</table>

Then, the relation between ethanol purity level with contact time is shown in Figure 5.
Figure 5 shows the optimal contact time of 60 minutes which is able to increase the level of ethanol as 3.64% from purities 90% to 93.28%. The results of the study showed that the length of the mixing time effects the amount of ethanol that can be adsorbed by adsorbent. The longer the time stirring, the more ethanol and water is sequestered. This is because the contact time between the solution and adsorbent increasingly, so that the mass transfer process of ethanol into adsorbent also increased [9].

Comparison of the amount of ethanol and zeolite in the process of adsorption distillation may affect purities ethanol which was obtained. If the amount of zeolite is more than the amount of ethanol and not only the water in the ethanol participating in but ethanol also joined. This would cause a reduction in the level of purity, instead if the amount of ethanol is more than the amount of zeolite and water content in the ethanol could not be entirely adsorbed by the number of the zeolite. Comparison of the composition of the ethanol and zeolite used in this research is only specified 2:1. This may cause a significant rise in the level of purity of ethanol. Therefore to get purities more optimum the suitable comparison of ethanol and zeolite need to be determined.

The process of soaking the zeolite in the ethanol before the process of adsorption distillation also allows affect purities ethanol obtained. Ever soaking of course has influence in increasing the level of purity. The shorter time zeolite was soaked in ethanol then the adsorption of water in the ethanol also the less that cause water content does not fully traps by zeolite, rather more long time zeolite was soaked in ethanol then the amount of water that increased accompanied with the amount of ethanol that participate in [2]. In this research there wasn’t any soaking step. This is also may cause an increase in the level of purity ethanol not significant, which is 3.64%. The process of soaking the zeolite in ethanol is important and the soaking time variation has been applied in order to get the optimum purity levels. The results of the test using Gas Chromatography shown in Figure 6.
Figure 6. The results of the Distillate Ethanol Test by the Variations of Contact Time

Figure 6 shows qualitative purities of ethanol, the best can be seen through the highest. Figure 6 shows that ethanol with the highest purity levels which has been indicated by the highest peak.

4. Conclusion
Chemical and physically activation affect the ratio Si/Al, analysis showed the ratio of the natural pahae Zeolite Si/Al of 3.03 (mordenite zeolite) so that the natural pahae zeolite is classified on the type of silica zeolite which has a range of the ratio between 2 - 5 and selective in adsorbing water vapour (H₂O). The optimum contact time required to increase the level of ethanol was 60 minutes with a percentage increase of ethanol by 3.64% (concentration of early 90% to 93.28%).

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References
CERTIFICATE

d this is to certify that

SUSILAWATI

has participated as

Oral Presenter

in SEMIRATA - International Conference on Science and Technology (ICST) 2018
"The Role of Science and Technology to Strengthen National Unity and Competitiveness"
held on May 4-6th, 2018 at Medan International Convention Center (MICC), Indonesia

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