Synthesis of zeolite from rice husk ash waste of brick industries as hydrophobic adsorbent for fuel grade ethanol purification

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Abstract. A lot of researchers have devoted on ethanol utilization as renewable energy to substitute petroleum based gasoline. When ethanol is being used as a new fuel candidate, it should have at least of 99.5% purity. Usually produced via sugar fermentation process, further purification of ethanol from other components in fermentation broth to obtain its fuel grade is a crucial step. The purpose of this research is to produce synthetic zeolite as hydrophobic adsorbent from rice husk ash for ethanol-water separation and to investigate the influence of weight, adsorption time and initial ethanol concentration on zeolite adsorption capacity. This research consisted of rice husk silica extraction, preparation of hydrophobic zeolite adsorbent, physical characterization using SEM, EDX and adsorption test for an ethanol-water solution. Zeolite with highest adsorption capacity was obtained with 15:1 alumina silica composition. The best adsorption condition was achieved when 4-gram hydrophobic zeolite applied for adsorption of 100 mL of 10% (v/v) ethanol-water solution for 120 minutes, which resulted in ethanol with 98.93% (v/v) purity. The hydrophobic zeolite from rice husk ash is a potential candidate as an efficient adsorbent to purify raw ethanol into fuel grade ethanol. Implementation of this new adsorbent for ethanol production in commercial scale may reduce the energy consumption of that usually used for the distillation processes.

1. Introduction

Indonesia has a diverse energy potential, both from fossil energy and non-fossil energy. Fossil energy sources include petroleum, natural gas, coal, and coal bed methane (CBM). Indonesia also has relatively large non-fossil energy sources, which are mainly water and geothermal. But its utilization is still less than the current potential. As clearly stated in the Blueprint of the Ministry of Energy and Mineral Resources of the Republic of Indonesia, the Indonesia’s existing petroleum oil reserves is about 9.1 billion barrels while the current annual production of 387 million barrels. With this condition, the current oil reserves will be exhausted in the next 23 years [1]. Also, the currently operated refinery infrastructures can only produce domestic fuels, which meet about 56% of the national fuel needs. Therefore, it is necessary to find alternative energy sources as substitutes to fossil fuel. One of
the alternative to gasoline is ethanol, which can produce from biomass in large scale.

The ethanol used as a fuel is called fuel grade ethanol (FGE) should have at least 99.5% purity and an octane number of 118 [2]. The fuel grade ethanol can be used as fuel either in a pure state or its mixture with gasoline at various concentrations [3]. Indeed, the presence of water in fuels, even at the lowest content, is highly undesirable. Therefore, water separation from ethanol mixtures becomes technological problem, especially in taking into account the azeotropic liquid vapors equilibrium relation. The azeotrope composition of the ethanol-water mixture is 95.63% ethanol and 4.37% water (by weight). Ethanol boils at 78.4°C, while water boils at 100°C, but the azeotrope boils at 78.2°C, which is lower than either of its constituents. The conventional method to solve the azeotropic problem is through azeotropic distillation. However, it consumes a large amount of energy. Therefore, it is necessary to develop more efficient and economical separation methods, which can combine with the conventional distillation or fermentation processes, such pervaporation with porous membranes [4] or adsorptive separations either in vapor phase [5] or liquid phase [6].

Concerning the heterogeneity of their crystal structure and specifically due to their molecular sieving capability, zeolites have been proven to be the most suitable adsorbents for separation of water-ethanol mixtures. The superiority is on the side of the 3A molecular sieves having a crystal structure which allows only the water molecules with molecular size 0.265 nm to penetrate inside the zeolite micropores. The other possibilities are that on the side of other dealuminated (highly hydrophobic silicalites) [9]. These zeolites have silica-to-aluminum ratio n = SiO2/Al2O3 > 100 [11]. In contrast to the 3A molecular sieves, the conventional 5A zeolite does not separate ethanol and water molecules. Both ethanol and water molecules can penetrate inside the zeolite micropore volume (the molecular size of ethanol is 0.446 nm [8]). But ethanol can absorb because high silica content of zeolite and its known as hydrophobic properties. Zeolite hydrophilic/hydrophobic property mainly depends on the Si/Al ratio, i.e., zeolitic hydrophilic property increases as the aluminum content in the zeolite framework increases and vice versa [12]. Hydrophobic/hydrophilic nature of zeolites also appears to depend on their framework structure [13]. Pure siliceous zeolite beta has been reported to be much more hydrophobic than silicalite-1 and the other siliceous 12-numbered ring zeolites, even though they contain almost no aluminum. Regular Si/Al-zeolites have adsorption capacities for alcohols/water in the following order H2O > methanol > ethanol > propanol, whereas silicalites are expected to give the reversed order of adsorption [14].

Some the crystalline forms of silica encountered in nature and some others exist as synthetic forms which extremely have no natural counterpart. Silicalite is a new hydrophobic crystalline silica molecular sieve, which its crystal structure is similar to zeolite ZSM-5. As a consequence, it can consider as the Al-free analogs of ZSM-5. Due to large surface area and pore volume, silicalite has good adsorption capacity. The competitive adsorption of a binary mixture (e.g. water and alcohols) on silicalite molecular sieve has shown that hydrophobicity increases with decreasing of the Na2O content of the adsorbent. This fact can consider as an advantage of silicalites compared to ZSM type zeolites [15]. The influence of alkali metal cations on the stability of silicalite is as Li+>Na+>K+>Rb+>Cs+, while particle size and morphology increase vice versa [16]. This adsorbent has a very beneficial hydrophobic and organophilic characteristic, which makes it suitable to use in selective adsorption of some organic materials from water, either in liquid or vapor phases [17]. Therefore, the synthesis of this material will be desirable due to its excellent potential for separation of polar organic compounds from gaseous or liquid mixtures (e.g. separation of small amounts of ethanol from fermentation broth). Due to the abundant availability of domestic resources used in this synthesis, the commercial production of this material is considered to be economical. This paper presents the synthesis of zeolite from rice husk white ash obtained from brick manufacturer waste and its capacity to absorb ethanol from the ethanol-water mixture. Rice husk ash highly potential as the raw material for zeolite production due to its high silica content (±94.5%) [18], less undesirable impurities and large surface area [19].
2. Materials and Method

2.1. Materials

The white rice husk ash used in this research was a donation from a brick manufacturer in Lampung-Indonesia. Technical grade ethanol (70% v/v), reagent grade sulfuric acid (98% w/w), sodium hydroxide crystal (75% w/w) and distilled water purchased from Indrasari Semarang. And the alumina hydroxide as the aluminum source obtained from Multi Kimia Raya Semarang. Zeolite synthesis

The hydrophobic zeolite prepared by mixing sodium silicate and sodium aluminate. White rice husk ash was initially dried in an electric oven at 105°C to reduce the moisture content to no higher than 10% (w/w). The dried ash was then ground with a mortar and sieved to obtain 300 um ash particles. Ten grams of rice husk ash was vigorously mixed with 10 M aqueous sodium hydroxide in a Pyrex glass reactor at 120°C under reflux for several hours to produce sodium silicate. Further, the slurry was then heated at 350°C for 4 hours until it turns into solid. Then the solid was dissolved in 100 mL of aqua dest and allowed to stand for 12 hours. Preparation of sodium aluminate done by dissolving 20 grams of NaOH crystal into 100 mL of aqua dest with continuous stirring. The NaOH solution heated to 100°C. After the NaOH solution reaches 100°C, 8.5 grams of Al(OH)₃ was gradually added into the solution for 20 minutes until the crystal completely dissolved. Sodium silicate and sodium aluminate mixed with a 5:1, 10:1, and 15:1 Si/Al ratio. The mixture was then dried at 150°C for 3 days and adjusted its pH with concentrated H₂SO₄ to a pH below 10. The mixture was re-dried and further ground to obtain uniform products.

2.2. Characterization and adsorption test of zeolite

The morphology of the zeolite was characterized using scanning electron microscope (SEM). The adsorption test of ethanol was carried out to determine the ability of zeolite as a hydrophobic adsorbent to produce fuel grade ethanol. The variables studied in this study were the adsorbent weight, adsorption time, and initial ethanol content. As much as 100 ml ethanol solution with 7.5%, 10%, and 12.5% (v/v) concentration was prepared from 70% (v/v) ethanol and each poured into a 500mL beaker glass. Then, 4, 8, and 12 grams of the synthesized zeolites introduced into the ethanol solution. The zeolite-ethanol solution mixtures left for 60 90, and 120 minutes to allow adsorption of ethanol molecules onto zeolites. Then, the zeolite separated from each solution. The zeolite adsorption capacity indirectly determined by measuring the refractive index of the ethanol solution by using the refractometer.

3. Results and Discussion

3.1. The morphology of zeolites

The SEM analysis was used to observe the microstructure of the surface of rice husk ash where main material of zeolite hydrophobic. The observed microstructures of zeolite particle with Si/Al ratio of 5:1, 10:1 and 15:1 depicted in Figure 1, Figure 2 and Figure 3. Also, the elemental analysis of the zeolite from the EDX analysis presented in Table 1.

Figure 1 and figure 3 show the uniformity of shapes of hydrophobic synthetic zeolite with the pore diameters 0.3-1μm and 0.05-0.01μm, respectively. Zeolite with Si/Al ratio of 15:1 (Figure 3) had the smallest pore diameter or largest specific surface area and more porous nature of X-type zeolite so that it is suitable for use as a hydrophobic adsorbent [20]. In contrast to that, the zeolite with Si/Al ratio of 10:1 (Figure 2) is rich in pores 0.01-1.5 um diameter. The particles were non-uniform in size and shape with some crystals apparently fused together to form agglomerate particles. The particle size of isolate crystal from SEM micrograph was approximately 2μm. This larger pore diameter may suggest the zeolite has less adsorption capacity due to the smaller specific surface area as compared to the former zeolites.
The EDX analysis reveals that for zeolites obtained from raw materials with Si/Al ratio of 5:1, 10:1 and 15:1, the actual Si/Al ratio in the zeolites were 5.67, 12.52 and 18.47, respectively. This fact shows that the Si/Al ratios in the zeolites reasonably higher than expectation. The zeolite with Si/Al ratio of 12.52 was likely to be $\text{Na}_6.6(\text{AlO}_2)_{6.6}(\text{SiO}_2)_{89.4}$ or ZSM-5 type MFI, while zeolite with Si/Al ratio of 18.47 was expected to be $\text{Na}_4.8(\text{AlO}_2)_{4.8}(\text{SiO}_2)_{91.2}$ or another ZSM-5 type MFI [20]. The zeolite with Si/Al ratio of 18.47 will be more suitable for ethanol adsorption from ethanol-water mixture [11]. Although all adsorbents are distinctly hydrophobic, the ethanol enrichment in the adsorbed phase changes drastically. Only those adsorbents with a small channel system (ZSM-5) have practical potential for hydrophobic separation [20]. The sodium content in the zeolite was the lowest for zeolite with Si/Al ratio of 1:15, while no significant different in sodium content observed for zeolite with Si/Al ratio of 5:1 and 10:1. This fact is mainly due to the higher concentration of sodium content in the reactant mixture during the fusion treatment [21]. In the case of a high content of (AlO4)- -Na+ dipoles in the cavities, the first water molecules are strongly localized on these dipoles and are the basis for the formation of the associates. These structures hinder the adsorption of the ethanol molecules on the oxygen walls of the cavities [20].

![Figure 1. Image of zeolite with Si/Al 5:1 with 3000× magnification](image1.png)

![Figure 2. Image of zeolite with Si/Al 10:1 with 3000× magnification](image2.png)

![Figure 3. Image of zeolite with Si/Al 15:1 with 3000× magnification](image3.png)

| Elements | Zeolite Si/Al: 5:1 | Zeolite Si/Al: 10:1 | Zeolite Si/Al: 15:1 |
|----------|-------------------|-------------------|-------------------|
| O        | 40.81             | 41.55             | 44.45             |
| Si       | 27.11             | 19.41             | 35.83             |
| Al       | 4.76              | 1.55              | 1.94              |
| Na       | 12.87             | 12.91             | 3.72              |

3.2. Effect of initial ethanol concentration

The adsorption capacity of zeolite can test through dynamic adsorption test. In the industry, fermentation of glucose using Saccharomyces cerevisiae may yield fermentation broth with 7 – 12% (v/v) ethanol content [22]. Therefore, the zeolites obtained in this work were tested their adsorption capacity using 4-gram zeolite and 100 mL ethanol solution with initial ethanol concentrations varied between 7-12% (v/v) for 120 minutes. The results of ethanol adsorption test on zeolites with various Si/Al ratios and initial ethanol concentrations depicted in Figure 4.

In an adsorption system, the behavior of the adsorbed phase differs significantly from the bulk phase. In the bulk free liquid, the water molecules associated in clathrates. The first ethanol molecules can fill the cavities of the clathrate structure. The positive deviations from Raoult's law for the activity coefficients in the bulk phase caused by repulsive forces between the ethanol molecules and the water clathrates. With higher ethanol content, a pseudo two-phase system of the clathrates and a random
ethanol-water mixture exists. However, as the concentration of ethanol increases the degree of association is lower because of the decreasing number of hydroxyl groups in the bulk phase [20].

Figure 4. Effect of initial ethanol concentration on ethanol adsorption capacity

Figure 4 confirms that zeolite with Si/Al ratio of 15:1 possesses highest adsorption capacity compared to the other zeolites with less Si/Al ratios for all initial ethanol concentrations studied. With lowest sodium content, the water molecules were not trapped inside the zeolite pores and did not further interact with sodium cations surrounding the zeolite pores [23]. Highest ethanol concentration (98.93% v/v) can obtain when this zeolite was used to absorb ethanol solution with 10% (v/v) initial concentration. The least ethanol adsorption capacity observed for zeolite with Si/Al ratio of 10:1. This zeolite is likely to be hydrophilic as its ethanol adsorption capacity decreases with the increase of initial ethanol concentration. Surprisingly, the adsorption capacity of zeolite with Si/Al ratio of 5:1 increases with initial ethanol concentration. This finding agrees well with previous work reported in the literature that dealuminated [9], or highly hydrophobic silicalites [9] has the higher preference to absorb ethanol rather than water molecules. Gaara and Akporiaye also reported that the activity of Y-zeolite increase in the yield with decreasing aluminum content suggesting the rise of hydrophobicity of dealuminated zeolite [24].

Figure 5. Effect zeolite weight on ethanol adsorption capacity
3.3. Effect of zeolite weight
This study was conducted by adsorption of 12% (v/v) ethanol solution onto zeolites for 120 minutes at various zeolite weights. Figure 5 presents the superiority of zeolite with Si/Al ratio of 15:1 to adsorb ethanol compared to the other zeolites. However, no significant adsorption capacity differences between zeolite with Si/Al ratio of 15:1 and that with Si/Al ratio of 5:1 observed. There was also noticeable phenomenon is that, when the zeolite weight reached a certain value, a gradual decline in ethanol concentration in the products appeared. Ivanova and coworkers also found that as the zeolite amount increases, the amount of ethanol adsorbed onto zeolite clinoptilolite pore surface gradually decreases [25]. a similar result was reported by Sumin et al. [26] on the adsorption of carbon dioxide using hydrophobic zeolite. On the contrary, an improvement in ethanol concentrations with the increase of zeolite weight observed for zeolite with Si/Al ratio of 10:1.

3.4. Effect of adsorption time
Three different adsorption times were chosen to study the effect of time on the adsorption of ethanol onto zeolites with three different Si/Al ratios. As shown in Figure 6, the ethanol concentration increases linearly with adsorption time on to zeolite with Si/Al ratio of 15:1, which is a high adsorptive capacity zeolite. Adsorption time only slightly affected the ethanol concentration of the product for zeolite with Si/Al ratio of 5:1. However, a different pattern was found for zeolite with zeolite with Si/Al ratio of 10:1.

As the adsorption time increases from zero to 90 minutes, the ethanol concentration in the product also increases. However, further increase of adsorption time using zeolite with Si/Al ratio of 10:1 reduces the ethanol concentration in the product. This phenomenon suggests desorption of ethanol from zeolite pores surface at long adsorption time. For particles with low adsorptive capacity, before the particles get saturated, the adsorption capacity increases with time. As time propagates, however, the zeolite particle gets saturated, and the amount of adsorbed ethanol molecules decreases gradually [26].

4. Conclusion
Based on the experimental data, it can conclude that zeolite with Si/Al ratio of 15:1 is the most suitable adsorbent for ethanol. No significant effect of initial ethanol concentration and zeolite weight on the product ethanol concentration. Longer adsorption time results in higher ethanol concentration of the product for adsorption using zeolite with Si/Al ratio of 5:1 and 15:1. Different trends observed for the effect of initial ethanol concentration, zeolite weight and time during adsorption of ethanol using
zeolite with Si/Al ratio of 10:1. A relatively good adsorption condition was adsorption of 10% (v/v) ethanol solution using 4 grams of zeolite with Si/Al ratio of 15:1 for 120 minutes to obtain the product containing 98.93% (v/v) ethanol.

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