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Ethanol Purification Using Activated Natural Zeolite

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Abstract

Bio ethanol is one of the potential fuels in the future. However, ethanol in water mixture has an azeotropic concentration of 95.6 wt. %, which makes it difficult to purify further. The common method of purification is by using an azeotropic distillation column, which requires an intensive energy and an addition of specific solvent. In this study, ethanol purification is done using an adsorption column packed with zeolite Raschig rings. The natural zeolite ring was modified beforehand using the NaOH solution to enhance the material's water adsorption performance. The ethanol purity can reach more than 99% with the modified zeolite packing. The modification also increases the saturation time of the packed bed column, thus making it more efficient.

Abstract

Pemurnian Etanol dengan Zeolit Alam Teraktivasi. Bio ethanol adalah salah satu bahan bakar potensial di masa depan. Namun campuran etanol dalam air memiliki titik azeotrop pada konsentrasi 95,6 % berat, sehingga sulit untuk dimurnikan lebih lanjut. Metode umum yang dipakai dalam pemurnian etanol adalah menggunakan kolom distilasi azeotropik yang membutuhkan energi yang intensif dan penambahan solven tertentu. Pada penelitian ini, pemurnian etanol dilakukan dengan kolom adsorpsi dengan bahan isian cincin zeolite di dalamnya. Zeolit alam sebelum digunakan dimodifikasi dengan larutan NaOH agar kemampuan penjerapan (adsorpsi) air menjadi meningkat. Kemurnian etanol dapat mencapai lebih dari 99% dengan zeolite termodifikasi. Modifikasi ini juga meningkatkan waktu saturasi kolom sehingga kolom bisa dijalankan dengan efisien.

Keywords: ethanol purification, adsorption column, modified zeolite

1. Introduction

The demand for renewable fuels is increasing rapidly. Biofuel will be blended with petroleum-based fuel to increase its quality as well as fulfilling the environmental soundness. Before we can blend biofuels with commercial fuels, it must have low water content. With regard to bio ethanol obtained from a fermentation process, the water content is still relatively high and difficult to remove due to the azeotropic properties of the mixture.

Many efforts have been made to remove water from an ethanol-water mixture, including processes, such as azeotropic distillation using solvents or entrainers [1,2], liquid adsorption using zeolites, alumina, resin and carbon [3-7], and membrane separation [8-10] to name a few. The distillation technique requires an intensive energy, while liquid adsorption consists of several stages in sequence. However, for a membrane separation process, even though the efficiency is high, it is expensive to build.

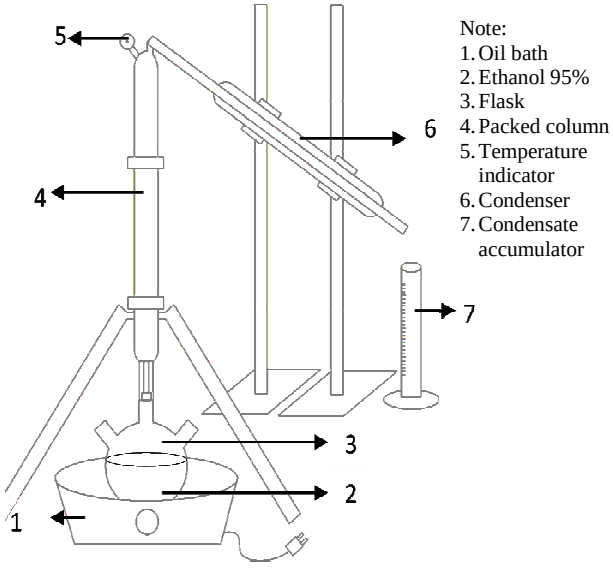
In this study, the ethanol-water mixture is purified using a semi-batch column adsorption. The column is packed with zeolite rings as water adsorbents. The low cost but efficient adsorbent is needed for mass production of bio ethanol.

2. Method

Natural zeolite taken from a local mining site (Bayah, in Klaten, Central Java) was crushed into powder and sieved before used. Some of the powder then underwent

a chemical modification using NaOH solution 3M at 90 ^{o}C for 36 hours. After washing and drying, the modified zeolite powder is ready to be used in preparing the Raschig ring packing. During packing preparation, water was added gradually into an equal mixture of zeolite and bentonite powder under continuous manual mixing to produce an extrudeable paste. The paste was then extruded to create a hollow tube with an outer diameter of 2.5 cm and an inner hole measuring 1.0 cm in diameter, the tube was carefully cut into ring shapes of 2 cm in length. The rings were oven dried and calcined at 700 ^{o}C for 1 hour. The solid materials were analysed using the XRD Multiflex Rigaku.

In ethanol purification as depicted in Figure 1, the packing was put inside a vertical tube of 5 cm in diameter and 40 cm in length. The tube was connected with three necked flask filled with low concentration of ethanol at the bottom and a condenser at the top. The ethanol solution



(a)

(b)

Figure 1. a. Apparatus for Ethanol Purification; b. Zeolite Packing

was boiled with an electric heater, the vapour was passed through the adsorbent bed and condensed. The liquid ethanol product was collected using an Erlenmeyer flask. The purified ethanol was sampled and analysed using the Gas Chromatography GC-FID Shimadzu 14-B in a specific time interval.

For determining the mass transfer coefficient, the purified ethanol in the column was modelled using the mass balance equation in an element volume ($S.\Delta z$) inside the bed with the bed bulk density of ρ_b and porosity of ε, while S (cm^2) is the bed area perpendicular to the ethanol vapour flow with the flow rate of F (g/s). The radial concentration distribution and axial diffusion are neglected. The water partial fraction (Y_A) in the gas phase is represented by Eq.(1).

$$\frac{\partial Y_A}{\partial z} - \frac{S.K_y.a}{F}(Y_A - Y_A^*) = \frac{S.\varepsilon}{F}\frac{\partial Y_A}{\partial t} \quad (1)$$

The mass fraction of water inside the packing (X_A, *g water/g solid*) is expressed by Eq.(2). Meanwhile, Eq.(3) shows the total concentration of water inside the column.

$$\frac{\partial X_A}{\partial t} = \frac{Ky.a(Y_A - Y_A^*)}{\rho_b} \quad (2)$$

$$Y_A^* = H.X_A \quad (3)$$

The mass transfer coefficient ($K_y.a$) and the Henry's constant (H) are determined by the Sum of Square Error (SSE) method.

3. Results and Discussion

Material characterization from the XRD analysis is shown in Figure 2. The NaOH treatment has some severe effects on the crystallinity. Some major peaks of the mordenite structure are reduced in intensity due to the treatment. Some new peaks are developed as well, which represents a new phase of zeolite due to the dilution and recrystallization of SiO4 and AlO4 as the building blocks.

The treatment not only alters the structure, but it also changes the cations content inside the solid. The NaOH treatment replaces the natural cations of Na^+, $Ca2^+$ and K^+ with a single cation (Na^+). The replacement of a larger cation Ca(II) with a smaller sodium ion can enlarge the pore opening as well, and therefore, allowing a faster mass transfer inside the zeolite cavity.

Figure 3 shows the concentration profile of ethanol after passing the column and condensed (an ethanol product). It shows that at the early stage, ethanol concentration is decreasing. This could be attributed to more ethanol molecules being adsorbed by the packing than water molecules. However, after 20 minutes, the concentration of ethanol products starts to increase. For the non-

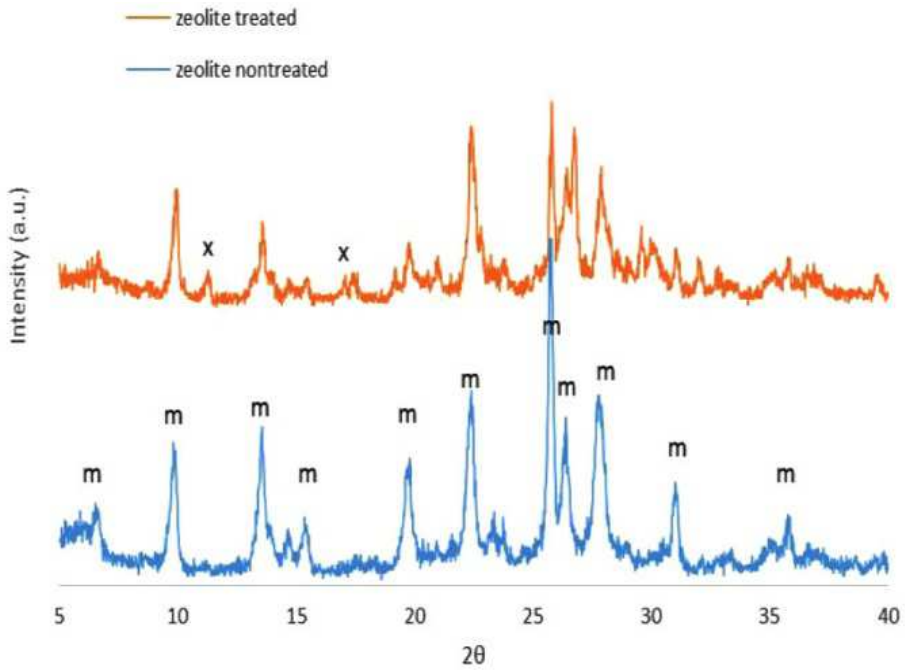


Figure 2. XRD Pattern of Zeolite before and After Treatment (m= mordenite, x= unknown)

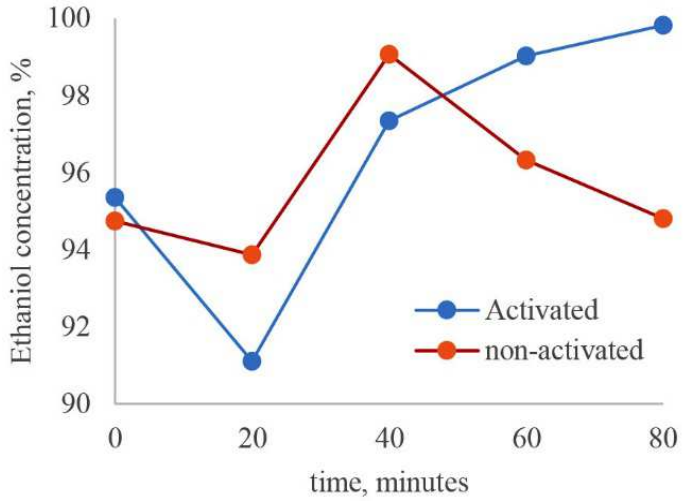


Figure 3. Concentration Profile of Purified Ethanol

activated zeolite, the profile reaches its peak at 40 minutes and then declines. This indicates that the packing is already saturated with water molecule. Meanwhile, for the activated one, the concentration continues to increase after 40 minutes, and it reaches 99.8% after 80 minutes.

The coefficients obtained from the simulation and the SSE values are listed in Table 1. It can be said that the activated zeolite packing has a faster mass transfer than the non-activated one due to a larger Ky.a. The affinity to water molecules increases dramatically after modification of the zeolite.

From the mass transfer simulation, a chart depicting the degradation of water concentration inside the column packing can be generated (Figure 4). The model fits the data well as indicated by a very low SSE values in Table 1. At the bottom of the column water concentration is at the highest and gradually decreases near the top of the column. By increasing the adsorption time, water concentration inside the column in any location will increased.

Table 1. Coefficients Calculated from the Simulation

Packing	H	Ky.a (1/s)	SSE ($x10^{-6}$)
Activated	0.018	0.0120	5.859
Non-activated	0.021	0.0029	5.765

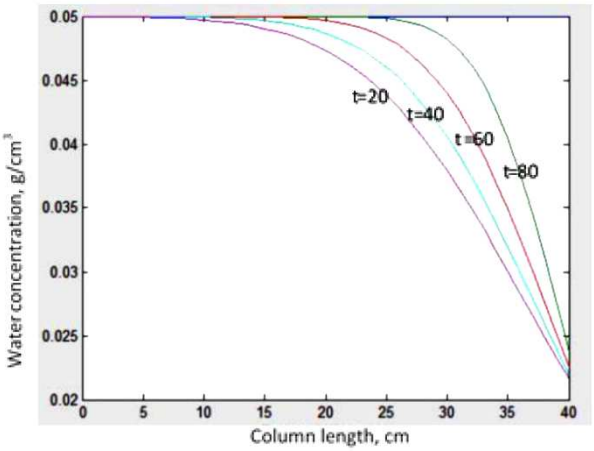


Figure 4. Water Concentration Profile Inside the Activated Zeolite Packed Column in Several Time Intervals

If the adsorption continues, then there will be a time when the concentration of the inlet will be equal to the outlet, which is called the breakthrough time. The breakthrough time needs to be determined, especially when up scaling the equipment from lab scale to industrial scale. Return to Figure 3, it can be said that the non-treated zeolite column has reached a breakthrough at 80 minutes because the output of ethanol concentration is already equal to the input. Meanwhile, the treated zeolite packing is still far from the breakthrough time.

4. Conclusion

Ethanol can be purified using vapour adsorption in the zeolite packed column. The NaOH treatment of zeolite can enhance the water uptake and improve the service time of the column. This method provides an efficient alternative for ethanol purification.

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