A Prospective of Coal Fly Ash Conversion to Mfi Membrane for High Grade Biofuels Purification

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Abstract. MFI is a structure of aluminosilicate zeolite mineral belonging to the pentasil family of zeolites. The current paper focuses on preparation of MFI zeolite from coal fly ash by hydrothermal process. Coal fly ash was utilized as the sources of silica. The as-synthesized zeolite was characterized by X-ray diffraction (XRD) to identify the structure and microstructure morphology observation by Scanning Electron Microscope (SEM) and adsorption-desorption analysis using nitrogen at 77 K. This kind of zeolite has a highly prospective to increase the purity of ethanol from technical grade become the fuel grade, catalyst, molecular sieve and adsorbent to reduce the emission gas.

1. Introduction
Coal is the oldest technique to run steam turbines for producing electricity. The major disadvantages of coal energy when it is burnt it releases harmful gases in the air, results in flue gas, fly ash and bottom ash which contain thorium, mercury and other metals. The disposal of such a huge quantity of ash has become a pressing issue. The main components of coal fly ash are oxides of silicon, aluminum, iron, and calcium, with lesser amounts of magnesium, sulfur, sodium, and potassium [1-3].

As one of the effective uses of coal fly ash, its conversion into zeolite was investigated. Recently, zeolite materials have attracted considerable attention because of a variety of technological and scientific applications, involving adsorption, membrane separation [4], ion exchange, membrane reactor, catalyst and transdermal drug delivery [5], anti-corrosive coating [6-9], Biofuel purification. Zeolite membranes potentially have better thermal and chemical stability than polymers and could thus be used under conditions in which current polymeric membranes are not suitable.

Zeolites are conventionally prepared by the hydrothermal method of the gel containing silica, alumina, cation, template and water [11]. Different types of silica are known to produce different types of zeolites from the same gel mixture [12]. Most of the silica sources used in the synthesis of zeolite are commercially available in the form of a solution, a gel, a fumed solid, a colloid, and an organic derivative such as tetraethylorthosilicate.

The disadvantages currently associated with zeolite membranes are mainly their high cost and complex fabrication procedure. Chemicals price such as silica sources give a major contribution to the production cost. [12]
Many researchers have reported that the zeolite crystals are produced from coal fly ash by an alkali hydrothermal reaction. However, the synthesis of MFI zeolite membranes using coal fly ash as the source of silica has not been reported. MFI-type zeolite membranes exhibit good separation performance and stability, which have been used for purification bioethanol by pervaporation [13]. The mixture of 95.6% ethanol and 4.4% water (percentage by weight) is an azeotrope with a boiling point of 78.2 °C and cannot be further purified by distillation. The membrane can break the water-ethanol azeotrope because separation is not based on vapor-liquid equilibrium. The separation in membrane is based on the size and shape of molecules. Membranes are also well-known as a hybrid membrane distillation process. This process uses a pre-concentration distillation column as first separating step. The further separation is then accomplished with a membrane operated either in vapor permeation or pervaporation mode. The membrane feed is vapor in vapor permeation process, and pervaporation process uses a liquid as membrane feed.

According to previous publication, the zeolite MFI membrane was able to enhance the purification of bioethanol from technical grade to fuel grade [13-14]. By using 10% fuel grade ethanol blend with gasoline could reduce emissions of carbon monoxide (CO) 25-30%, carbon dioxide (CO₂) up to 100%, nitrogen oxides (NOₓ) about 20%, volatile organic compounds (VOC’s) 30% or more, Sulphur dioxide (SO₂) and aldehydes [15-16].

In this study, the hydrothermal synthesis of MFI zeolite membrane from coal fly ash was investigated in alkali solutions. Characterization was conducted by X-ray diffraction to identify the structure, Scanning Electron Microscope for microstructure observation and physisorption to investigate the pore channels. The separation performance was tested for bioethanol separation and purification using pervaporation method.

2. Experimental Section

2.1. Preparation of silica from coal fly ash

The main raw material of coal fly ash samples was collected from Tarahan power plant, Indonesia. The fly ash sample was screened through 80 mesh sieves. Purification process was carried out to remove carbon, iron and reduce alumina. The remaining carbon was removed by calcinations process at 700 °C for 2 hours. The calcined fly ash was treated with 4M KOH and reflux with 3M HCl for 5 hours, then filtered and washed repeatedly with water then dried at 110°C overnight.

2.2. Synthesis zeolite MFI membrane

The Zeolite MFI membrane was prepared with asymmetry alpha alumina support with the smallest top pore size 100 mm by a hydrothermal method. The membrane was formed on the surface of the support by direct crystallization. The parent solution was prepared using Cation tetrapropylammonium (TPA) was used as organic template. It was formulated with fly ash silica, sodium silicate and NaOH with molar ratio 6.24Na₂O: 0.154Al₂O₃: 12.37SiO₂: 0.37TPABr: 100H₂O. All the materials were stirred 200 rpm at 313 K for 2 hr. α-alumina support was immersed in the parent solution for 1 hour at 313 K. Then carefully the solution and alpha alumina support inserted into a Teflon chamber in stainless steel autoclave then sealed. The crystallization process was conducted at 453 K for 24 hours in an autoclave without stirring. After the crystallization process completed, then as-synthesized membrane was washed using distilled water, followed by drying to remove water content from the membrane. Finally, the organic template was removed from the membrane by calcination process at 773 K for 5 hours with the increasing temperature 1 °C/min.

2.3. Characterization

Membrane structure was identified by using X-ray diffraction (XRD) using Cu K α radiation (Simadzu XRD-6000). Microstructure observation using Jeol Scanning Electron Microscope (SEM JED 2300).
Adsorption-desorption characteristic of MFI zeolite was studied using Autosorb-1 (Quantachrome, USA). The nitrogen adsorption-desorption isothermal was conducted at a relative vapor pressure $P/P_0$ from 0 to 1 by increment of 0.001. The Barret-Joyner-Halenda (BJH) pore size distribution was analyzed.

2.4. Bioethanol purification

The pervaporation test of as-synthesized zeolite MFI membrane for purification of bioethanol was conducted at room temperature. The schematic pervaporation test setup is shown in Figure 1. Technical grade bioethanol (90%) was used as the feed.

![Figure 1. Membrane pervaporation system for ethanol purification.](image)

3. Results and discussion

The composition of fly ash from Tarahan power plant, Indonesia is shown in Table 1. The main components of coal fly ash are oxides of Si and Al. Silica and alumina content of the sample was 58.70% and 25.60% respectively. The XRD pattern of coal fly ash is shown in Figure 2.

| Content | Composition (wt. %) |
|---------|---------------------|
| SiO$_2$ | 58.70               |
| Al$_2$O$_3$ | 25.60       |
| Na$_2$O | 1.05               |
| TiO$_2$ | 2.54               |
| Fe$_2$O$_3$ | 4.15          |
| K$_2$O | 0.98               |
| CaO    | 1.06               |
| MgO    | 1.72               |
| MnO    | 0.03               |

According to the XRD pattern as shown in Figure 2, the coal fly ash content quartz (SiO$_2$) as the main crystalline substances.

Figure 3 is the XRD pattern of as-synthesized MFI zeolite membrane. Peak of quartz was reduced significantly, changed with a peak of MFI structure. The characteristic diffraction peaks in the range of 2 theta 7–9 degree and 23–25 degree reveal that a pure MFI phase is formed.
Figure 2. XRD pattern of fly ash silica

Figure 3. X-ray diffraction pattern of as-synthesized MFI zeolite membrane.

Figure 4 shows the adsorption-desorption isothermal curve of MFI zeolite materials revealed micro porosity as a sharp increasing curve at $P/P^0$ at lower than 0.1 due to filling of micropores. The hysteresis loop at $P/P^0$ (mesoporous area) followed the characteristic of Type IV isotherms was caused by capillary condensation where the size of the pore at the mouth less than pore inside. The narrow Barret-Joyner-Halenda (BJH) pore size distribution of as-synthesized MFI zeolite is shown in Figure 5. The average pore size was about 0.55 nm.
Figure 4. The nitrogen adsorption-desorption isothermal of MFI zeolite

Figure 5. BJH pore size distribution of as-synthesized MFI zeolite
Figure 6. SEM micrograph of the top surface MFI zeolite membrane (left) and cross section (right)

Figure 6 shows the SEM micrograph of MFI membrane. From the cross section of SEM micrograph in Figure 6 (right side), the thickness of the membrane was about 50 µm. Top surface of membrane possesses high porosity and surface roughness.

The pervaporation test of bioethanol was carried out using technical grade 90% ethanol at room temperature. The separation factor was ca.11 delivered the concentration of bioethanol at permeate was 99%. According to ASTM D4806 standard of fuel grade ethanol, the zeolite MFI membrane was able to purify the concentration of bioethanol from technical grade (90%) to fuel grade.

4. Conclusion
Sila with the purity of 58.50% and 25.6% alumina could be produced from coal fly ash. The coal fly ash was able to be utilized as silica and alumina sources for synthesizing MFI zeolite membrane.

The MFI zeolite possesses micropores channel with a narrow pore size distribution. The average BJH pore size was ca.0.55 nm. Nitrogen adsorption-desorption characteristics contained the hysteresis of Type IV isotherms due to capillary condensation where the size of the pore at the mouth less than pore inside.

The Zeolite MFI membrane was able to purify the bioethanol, which cannot perform by distillation, from technical grade (90%) to fuel grade (99%), the separation factor around 11.

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