Mixed matrix membrane of alginate zeolite crosslinked by PVA for separation of CO$_2$/CH$_4$

Syardah Ugra Al Adawiyah
Politeknik ATI Makassar
E-mail: syardah.ugra.su@gmail.com

Abstract. Mixed Matrix Membrane Alginate Zeolite Crosslinked by PVA for Separation CO$_2$/CH$_4$ was studied. Alginate/Zeolite/PVA mixed matrix membrane were prepared by solution casting. The research started by synthesis of Alginate/Zeolite/PVA membrane. The PVA 0.1% crosslinking alginate zeolite membrane (1:0.2) was successfully synthesized. The membrane were characterized by Fourier Transform Infrared (FT-IR) and Barret Joyner Hallenda (BJH). The membrane permeability and selectivity of CO$_2$ and CH$_4$ were investigated. The effect of zeolite on the performance and the thickness of membranes of gas separation were analyzed. The result of permeability and selectivity show that membrane can flow CO$_2$ and resist CH$_4$. The effect of zeolite mass increasing on permeability of CO$_2$. The thickness of membrane influenced the flux of CO$_2$ gas. CO$_2$ permeability increased simultaneously with a decrease of a membrane thickness. According BJH result, pore diameter of membrane is 3.54 Å, while kinetic diameter of CO$_2$ is 3.3 Å and kinetic diameter of CH$_4$ is 3.8 Å. This was explained performance of membrane was molecular sieving.

1. Introduction

Global warming is one of the major problems that face humanity. Global warming is caused by the emission of greenhouse gases, of which the main component is carbon dioxide (CO$_2$). CO$_2$ emissions have dramatically increased in the last 50 years, and are still continually increasing each year [1]. The technology of membrane has begun to be applied for the separation of CO$_2$ from natural gas. The advantages of this technology is a simple process, convenient, environmentally friendly, low energy consumption and operating costs [2]. His technology is commercially available for gas purification in 1980. Over the past years several studies are conducted in searching optimum membrane materials, membrane casting techniques and membrane module configurations for gas separation. Efficiency of membrane decreases with the passage of time which is the biggest challenge for industries [3].

In this method, a few components of the gas transported through a thin layer of membrane. Transport of each component is controlled by the partial pressure difference on the membrane. The membranes that can be used for gas separation have 2 types, i.e. porous membrane and non-porous membrane [4]. The transport mechanisms that can occur in gas permeation along the porous membrane is a bulk flow, molecular diffusion and molecular sieving [5].

The usefulness of alginate based on three main properties, the ability to: 1). soluble in water 2) increasing the viscosity of the solution to form a gel. 3). forming film and fiber [5]. Sodium alginate (NaAlg) is a cheap, stable and easily available polymer containing carboxyl groups [6]. NaAlg has very high hydrophilicity resulting from its carboxyl and hydroxyl groups [7], which is beneficial for
the solubility of CO$_2$ in the membrane since water is needed for the preferential CO$_2$ permeation. Therefore, NaAlg should be a good candidate for CO$_2$ separation membrane materials [8].

Zeolite minerals, also known as natural sedimentary or natural occurring zeolites, are mainly composed of aluminosilicates with a three-dimensional framework structure bearing AlO$_4$ and SiO$_4$ tetrahedral. Natural zeolite mineral is suitable for use as the major component in the fabrication of mineral based membrane partly because it does not swell in water and easily forms a suspension for coating membrane on porous support [9]. Zeolite pore structure makes zeolites are often used as a tool for separating a smaller or larger substance from other substances. In use as a separator, zeolite is often synthesized then modified structure that can filter and separate the molecules of substances [10].

Polyvinyl alcohol (PVA) is an inexpensive polymer with an excellent film-forming ability used in membrane separation, as a fuel-cell electrolyte and in biological applications. PVA has a repeating hydroxyl group that makes it hydrophilic and offers good compatibility in aqueous solutions PVA induces extensive swelling in water, which decreases its mechanical stability. One way to improve membrane stability and mechanical properties in aqueous solutions is to incorporate an inorganic filler into the polymer matrix [11].

2. Experimental Section

2.1. Materials
Alginate, PVA, natural zeolite, CO$_2$ gas, CO$_4$ gas aquades, HNO$_3$, HCl, filter paper.

2.2. Instruments
Glassware, weigher, magnetic stirrer, petri dish, oven, and set of gas permeability test equipment, Infrared Spectrophotometer, and Surface Area Analyser such as BET and BJH.

![Schematic of gas permeability test equipment](image)

Figure 1. Schematic of gas permeability test equipment

2.3. Procedures

2.3.1. Zeolite activation. Natural zeolite crushed and sieved to 100 mesh screening passes. 20 g siftings washed with aquabidest. Then, the zeolite was dried at 110°C for 4 hours. Zeolite demineralized with a solution of 50 mL of 1 M HCl for 1 day. Furthermore, zeolite dealuminated with 50 mL of 8 M HNO$_3$ for 1 day. Zeolite oven at 110 °C for 4 hours and calcined at 600 °C for 3 hours.
2.3.2. Preparation of alginate-zeolite membrane and zeolite/PVA/alginate membrane. Materials such as alginate and zeolite dissolved in distilled water according to the composition specified (Table 1). Then stirred using a magnetic stirrer until homogeneous for 24 hours. Homogeneous mixture has been poured into a petri dish and then allowed to stand at room temperature to dry and peel. Membranes permeability tested using a permeability test equipment.

Table 1. Composition of Membrane

| PVA   | Alginate: Zeolite Ratio |
|-------|------------------------|
| 0.1%  | 1:0.1                  |
| 0.1%  | 1:0.2                  |
| 0.1%  | 1:0.3                  |
| 0.1%  | 1:0.4                  |
| 0.1%  | 1:0.5                  |
| 0.1%  | 1:0.6                  |

2.3.3. Permeability and selectivity. Single gas permeability of CO$_2$ and CH$_4$ were measured through all membranes by constant volume and variable pressure technique. Volumetric gas permeation rates were measured with soap bubble flow meter. The pressure difference of membranes were controlled at several pressure. The permeability test was repeated to the three different membrane samples and an average data was sermined. Pressure-normalized flux through the membrane is usually expressed as

\[
\frac{P}{L} = \frac{Q_{stp}}{A_m (P_l - P_o)}
\]  

where \( \frac{P}{L} \) is permeability (GPU, 1 GPU = 10$^{-6}$ cm$^3$ (STP)$s^{-1}$ cmHg$^{-1}$), \( Q_{stp} \) is flow rate at standard conditions (cm$^3$(STP)$s^{-1}$), \( A_m \) is membrane area (cm$^2$), \( P_l \) is inlet pressure (cmHg), and \( P_o \) is out pressure (cmHg).

Selectivity of membrane can be sermined by relative permeability of components CO$_2$ and CH$_4$

\[
\delta \frac{CO_2}{CH_4} = \frac{P/L(CO_2)}{P/L(CH_4)}
\]

3. Result And Discussion

3.1. Characterization of the membranes

FTIR characterization that was carried out on the alginate/pva/zeolite membrane showed at (figure 2).
Based on the analysis using the SEM (figure 3), the morphology of zeolite/PVA/alginate membranes is soft and dense. This figure shows a uniform distribution of zeolite inside the alginate matrix. This zeolite particles play a role in passing the gas through the membrane. In addition, the homogeneity of the zeolite can affect permeability and selectivity of gas in separation process.

Identification of surface area is done through fisisorpsi N\textsubscript{2} gas at 77 K using microanalyzer NOVA 1200 (Quantachrome) using BET method (Brunaur Emmet Teller).

![Figure 3. Analysis using the SEM](image)

Based on this analysis, zeolite/PVA/alginate membrane has a specific surface area of 23.421 m\textsuperscript{2}/g and can produce the good permeability and selectivity of gas. Identification pore diameter is done through fisisorpsi N\textsubscript{2} gas at 77 K using microanalyzer NOVA 1200 (Quantachrome) using BJH method (Barret Joyner Hallenda). Based on this analysis, zeolite/PVA/alginate membrane have a pore diameter of 3.54 Å, can produce good permeability and selectivity of gas.

### 3.2. Membrane permeability and selectivity

#### Table 2. Effect of zeolite loading for the CO\textsubscript{2} permeability using alginate-PVA-zeolite membrane

| Pressure (Psi) | Membrane 1:0,1 | Membrane 1:0,2 | Membrane 1:0,3 | Membrane 1:0,3 |
|---------------|----------------|----------------|----------------|----------------|
| 5             | -              | -              | -              | -              |
| 10            | -              | -              | -              | 3,15 x 10\textsuperscript{-2} |
| 15            | 4,6 x 10\textsuperscript{-2} | 1,92 x 10\textsuperscript{-2} | 2,4 x 10\textsuperscript{-2} | 6,28 x 10\textsuperscript{-2} |
| 20            | 5,77 x 10\textsuperscript{-2} | 55,7 x 10\textsuperscript{-2} | 243 x 10\textsuperscript{-2} | 278 x 10\textsuperscript{-2} |
| 25            | 45,7 x 10\textsuperscript{-2} | 11500 x 10\textsuperscript{-2} | |

#### Table 3. Effect of membrane thickness for the CO\textsubscript{2} permeability using alginate-PVA-zeolite membrane

| Pressure (Psi) | CO\textsubscript{2} Permeability (GPU) |
|---------------|--------------------------------------|
|               | Membrane 50 ml (0,1589 mm) | Membrane 40 ml (0,1267 mm) | Membrane 30 ml (0,0899 mm) |
| 5             | -          | -          | -              |
The permeability of CO\(_2\) through this membrane increase with the increasing of applied zeolite mass and increasing of applied pressure. Discontinuities in permeability test occurs at applied pressure of 25, 20 and 20 for membrane respectively. At applied pressure of 25 Psi, the CO\(_2\) permeability of membrane 1:0,2 is much highest than was reported for other membrane. From the four types of membrane composition used and the permeability value of CO\(_2\) gas, it can be concluded that the membrane composition 1:0,2 has the best quality compared to other membranes. The average permeability of the membrane and the high pressure can be applied to membrane used as an indicator of the membrane strength during permeability testing.

Using the composition 1:0,2, varying thickness used to see the effect of the thickness on the membrane permeability. Three variation of membrane thickness (0.0899 mm, 0.1267 mm and 0.1589 mm) are tested. In the permeability test using all membrane, the CO\(_2\) gas can pass through membrane when the pressure of 15 Psi, while the CH\(_4\) gas could not penetrate the membrane on some variation of the pressure until the membrane 0.0899 mm leak at a pressure of 25 Psi and 0.1267 mm, 0.1589 mm leak at pressure of 30 Psi. As shown at Table 4, the permeability of CO\(_2\) through this membrane increase with the increasing of applied pressure in all membrane and membrane with thickness 0.1267 mm showed the best permeability compare to other membranes.

4. Conclusion

CO\(_2\) permeability increased simultaneously with an increase of zeolite content in the polymer matrix. The thickness of membrane influenced the flux of CO\(_2\) gas. CO\(_2\) Permeability increased simultaneously with a decrease of membrane thickness. The PVA 0,1% crosslinking alginate zeolite membrane (1:0,2) shows the best permeability.

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