A study of gas permeation on a polymeric membrane: permeability, diffusivity, solubility, and its performance for H_2/CO_2 separation

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Abstract

The gas permeation on a polymeric membrane for H_2/CO_2 separation in accordance to the solution-diffusion mechanism was studied. A commercial Polyvinyl alcohol (PVA) and Polyamide (nylon-6) membrane were used for pure and mixed gas permeation experiment and the interaction effects of the permeance gas with these polymeric membranes were observed by determining transports parameter such as permeability coefficient (P), diffusion coefficient (D), and solubility coefficient (S). Two-steps experiments were carried out:(1) pure gas permeation of H_2 and CO_2, and (2) mixed gas permeation of H_2-CO_2 (30 % H_2 - 70 %-v CO_2). The operating pressure was varied in the range from 4 to 12 bars. Membrane performance on a gas separation was represented by permeation flux (J) and its selectivity factor ( ). The experiment result showed that solubility of CO_2 in PVA was greater than Nylon-6 membrane and decrease with an increasing operating pressure. Permeability and permeation flux of H_2 were higher at both two types of membrane while the selectivity of H_2/CO_2 of nylon-6 membrane was higher in compared to PVA membrane.

keywords: gas permeation, polymeric membrane, polyvinyl alcohol, polyamide, permeability, diffusivity, solubility, selectivity

1. Introduction

The increasing of gas emission such as CH_4 and CO_2 on the atmosphere due to extensive oil usage generates substantial greenhouse gases. They caused a serious problem such as the climate change due to global warming effect (Powell et al., 2006) and thus, it needs an appropriate method to reduce CO_2 emission (Gu et al., 2012, Brunetti et al., 2010, Merkel et al., 2010, Zhao et al., 2008). Morever an affordable, clean and reliable energy supply such as hydrogen, is a major global concern as the world's fuel composition increases rapidly due to increased industrialization and human population (Shao et al., 2009, Feng et al., 2002). So, there exists an urgent need to shift the world's consumption of energy from fossil fuel to renewable energy sources.

Among various separation methods, membrane technology have been proposed as the new methods to reduce gas emission from various sources like as coal combustion, power plant, and from vehicle exhaust gas as shown in Fig.1.
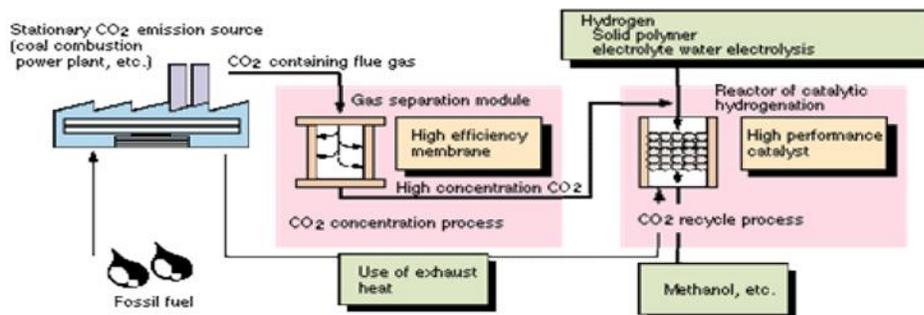

Figure 1. Recovery of CO_2 and its utililization by membrane separation

This figure shows that CO_2 is separated from stationary CO_2 emission sources and used as a synthesize gas for methanol production. Gas permeation membranes are well-established and fast growing in industrial technology. Membrane systems are effective at separating O_2 from N_2, CO_2 and H_2S from CH_4 and higher alkenes, and H_2 from N_2, hydrogen separation from its mixtures with other gases like methane, carbon monoxide and nitrogen in syngas ratio adjustment or in hydrogen recovery from hydrocarbons in refineries.

Although many types of membranes can be utilized for hydrogen purification or and CO_2 separation, polymeric membranes are preferred by and worthy of extensive study because of their lower material and fabrication cost, ease of processability, and capacity for long-term operation at relative mild operating temperatures and pressures. However, the separation process mechanism for gas separation with membrane was not clearly understood. Thus, the aims of this work is to study the separation process mechanism on pure and mixed gas permeation of H_2/CO_2 within a polymeric membrane and their interaction effects on gas separation performance. Firstly, the interaction effect between the permeance gas and PVA and Nylon-6 membrane will be studied by addressing special attention to the gas tansport parameters such as permeability,

diffusivity and solubility coeficient, and the membrane separation performance in term of permeation flux (J) and selectivity factor ( ) will be determined as respectively.

2. Fundamental

2.1. Gas permeation theory

Transport of gases through a dense polymeric membrane is usually described by a solution-difussion mechanism. In the solution-diffusion model (Wijmans et al.,1995, Li et al., 2013, Kim et al., 2011) the permeants disolve in the membrane material and then difuse through the membrane down a concentration gradient. This model is usually comprised of three steps: (i) the adsorption or the absorption at the upstream boundary commonly called the sorption step, (ii) the difussion through the membrane and (ii) the desorption or evaporation on the downstream side of membrane. The separation mechanism schematically shows in Fig.2.
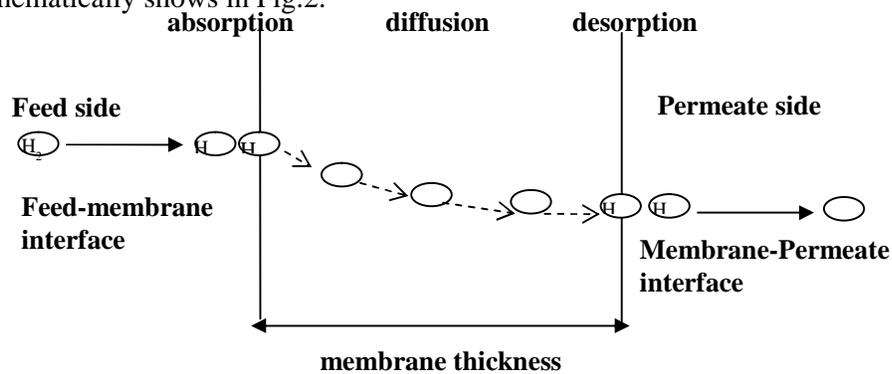

Fig. 2. Gas separation for non-pore membrane membrane

The driving force behind the transport process which involves sorption, difussion and permeation is the gradien concentration beetwen two sides of the membrane.

This process is described by Fick's laws of diffusiion which give the flux, J, in the direction of the flow, the rate of concentration change, dc/dt, at any point within the membrane. Fick's first law are described by eq (1).

$$J = - D \, (dc/dx), \quad dc/dt = D(d^2C/dx^2) \tag{1}$$

Where C is the concentration, t the time, D the diffusion coeficient and x is the position within the membrane down the concentration gradient.

After a certain permeation time the steady-state is reached which implies that the concentration is remaining constant at all points within the membrane and the flux may be described by eq.(2)

$$J = D (C_0-C_1)/l \qquad\qquad (2)$$

Where C_0 and C_1 are the permeant concentration on the upstream and the downstream side of the membrane thickness. In a system where a gas or a vapor diffuses through a membrane, the concentration may be replaced by gas partial vapor pressure, p_0 and p_1 on either side of the membrane, then J is usually descrfibed by eq.(3)

$$J = P(p_0-p_1)/l \qquad\qquad (3)$$

Where P is the permeability coefficient. In a rubbery polymer, the molecule sorption at low concentration is typically described by Henry's law [27] and if the diffusion cofficient is constant over the pressure range, the permeability coefficient may be rearranged to give the eq.(4)

$$P = D.S \qquad\qquad (4)$$

Where S is the solubility coefficient. To determine the permeability and the diffusion coefficient, the lag time is used as described in the following section.

2.2. Time-Lag method

When a gas is first admitted to one side of the dense polymeric sheet membrane both flow rate and gas concentrataion into the membrane vary with time. If the diffusing is continually removed from the low concentration side of the membrane, and the permeation time is high enough, then the steady-state is achieved and the curve of the amount of gas permeating through the membrane, Q, against time t, tends to be a straight line describe by eq.(5) [28-30] and it is shown in Fig.3.

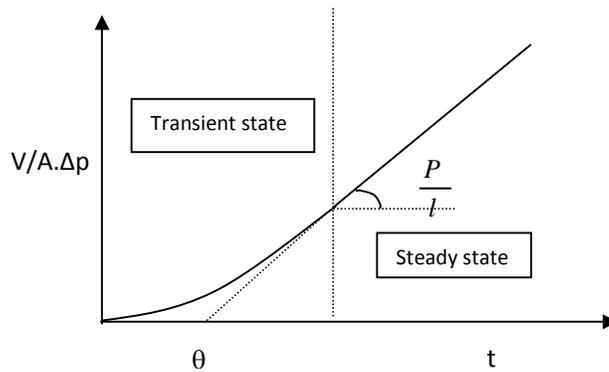$$Q_t = \frac{D.c_i}{\ell}\left[t - \frac{\ell^2}{6D}\right]$$ (5)

Fig.3. Gas permeation curve

According to Henry's Law, the relation of ammount of gas can be sorpbed has a proportional relation to its solubility and pressure as described by the following equation.

$C_i = S. p_i$ (6)

and the total amount of gas permeation fluxs, Qt, in cm^3 (STP).cm^2.s, can be be describes as:

$Q_t = V/A.$ (7)

Thus, by subtituting the eq.(7) into eq.(5) and by rearranging the eq.(2), (3), (4), (5), (6) and eq.(7), finally, we can get the final equation of gas permetion through a polymer membrane as described below.

$$\frac{V}{A.p_i} = \frac{P}{\ell}t - \frac{P}{6D}\ell$$ (8)

then by manipulating *P/l,* eq.(8*)* can be writedown as

$$\frac{V}{A.p_i} = \frac{P}{\ell}(t - \frac{\ell^2}{6D})$$ (9)

By plotted the V/A.p$_i$ on y-axis against t on x-axis, this gas permeation curve has a slope (*P/l*) and an intercept,   , commonly called lag time, on the t-axis given by

$= l^2/6D$ (10)

Regarding to this permeation curve, then the permeability coefficient (P) of permeate gas can be obtained by multiplying the slope with the membrane thickness. Where permeability coefficient is in $cm^3(STP).cm/cm^2s.cmHg$. The permeability coefficient is also given in Barrer (1 Barrer = $1x10^{-10}$ $cm^3(STP).cm/cm^2s.cmHg$. The solubility coefficient (D) in cm^2/s, can be determined from the intercept of permeation curve and can evaluated from eq.(10). Finally, the solubility coefficient, S, in $cm^3(STP)/cm^3(Polymer)$ cmHg, can be obtained from Eq.(4) or by dividing the permeability coefficient (P) with diffusivity coefficient (D).

3. Materials and Method

Commercial polyvinyl alcohol (PVA) and a linier type of polyamide membrane (Nylon-6) were used for pure gas and mixed gas permeation of H_2/CO_2. The thickness and effective area of flat disk PVA and Nylon-6 membrane are 50 μm and 14.7 cm^2, respectively. The moleculer structure of Nylon-6 and PVA are shown in Fig.4 .

Fig. 4. The moleculer structure of polymeric membrane: (a). Polyamide (Nylon-6) and (b). Polyvinyl alcohol (PVA)

Two stages experiment were conducted to compare the performance of PVA membrane and polyamide (Nylon-6) for pure and mixed gas separation of H_2/CO_2.

3.1. Pure gas permeation

Pure gas permeation of single gas of H_2 and CO_2 were performed using a constant-volume/variable-pressure method at a various feed pressure and at an ambient temperature of 25 ℃. The permeation gas apparatus for pure and mixed gas permeation shows in Fig. 5 below.
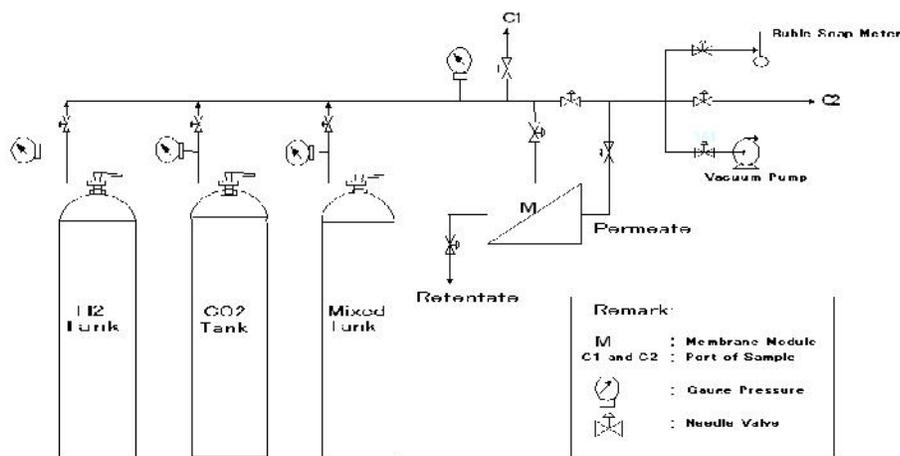
Fig. 5. Gas permeation system apparatus

The gas permeation system are comprises of a piping line, a soap-buble flow meter to measure the gas flux, Q_t, and a membrane module which is consist of a chamber that sealed onto a flast disk membrane via an O-ring and a non woven stainless stell as a membrane support. In order to keep the air-free condition in a gas permeation system before the gas permeation measurements, both the feed and the permeate sides were evacuated to a vacuum condition. Then by adjusting feed pressure, the permeation cell was pressurized with the gas of interest (H_2 and CO_2), so that a gas is allowed to permeate from the upstream to the down stream at atmospheric pressure. All measurements with that gas were then taken after a steady-state flux was observed. Fluxes were measured at pressures of 4-12 bars. The fluxes of H_2 and CO_2 were determined for each membrane. Permeability of the individual gases of each pressure was determined from slope of pure gas permeation curve, and the diffusivity coefficient was determined from its intercept and then the solubility coefficient was calculated according to eq.(4). The ideal separation factor i/j for pure gas permeation can be calculated by using the following equation (Morisato et al., 1999, Thomas et al., 2009).

$$a_{i/j} = \frac{(P/l)_i}{(P/l)_j} \tag{11}$$

3.2. Mixed gas permeation

A gas cylinder consist of H_2 and CO_2 with the composition of 30-v% H_2 and 70-v% CO_2 was used for mixed gas permeation. The operating pressures were varied in the range from 12 to 14 bars. Feed gas pressure were varied from 4 to 12 bar while the downside pressure was at atmospheric pressure. The mixed gas permeation experiment was conducted at room temperature. The experimental flowchart of pure and mixed gas permeation is shown in Fig.6.
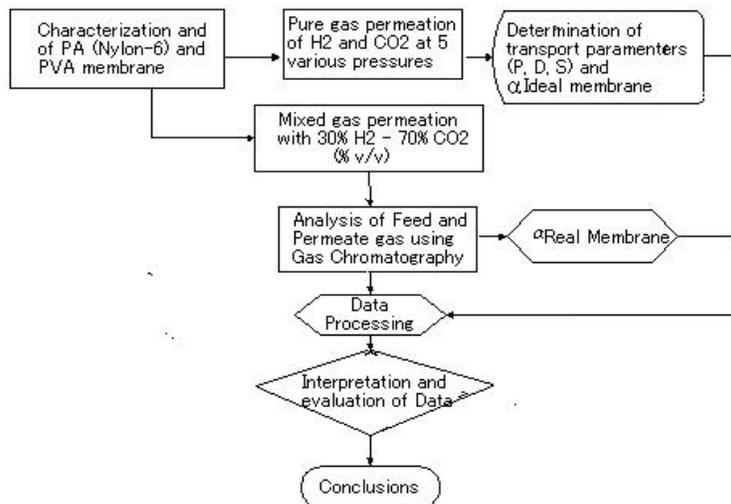

Figure 6. The experimental flowchart

Feed gas and permeate gas composition were analyzed by chromatography gas (GC). The fluks permation of mixed gas permeation can be obtained by measure of mixed permeant gas volume when a steady state condition is attained. Then the real separation factor of mixed gas permeation was calculated from the eq.(12)

$$a^*_{A/B} = \left[(y_A / y_B) / (x_A / x_B) \right] \qquad (12)$$

4**. Results and discussion**

4.1. Diffusivity, permeability and solubility coeficient of pure gas permeation

   Fig. 7 shows the experimental results of pure gas permeation of H_2 and CO_2 at various feed pressure. It is shown that permeability of H_2 and CO_2 for both two types of membrane increases with increasing of feed pressure. Permeate flux of H_2 and CO_2 for the PVA membrane higher than for the PA (Nylon-6) membrane. This is attributed to the fact that PVA membrane has a group of hydroxyl units (-OH), therefore PVA membrane more hydrophilic, and also (-OH) groups could make the PVA membrane more swollen, thus the gas molecules can easily absorbed and diffused through membrane. The gradient pressure also gave the great effect on the gas permeate. Generally, gas permeates increase linearly by increasing gradient pressure. The permeate flux of H_2 is much higher than CO_2 because it has a higher rate permeate *(P/l)* both on PVA and Nylon-6 membrane. Whereas the ideal selectivity ( ) for H_2/CO_2 on Nylon-6 and PVA membrane increases with an increasing feed pressure.
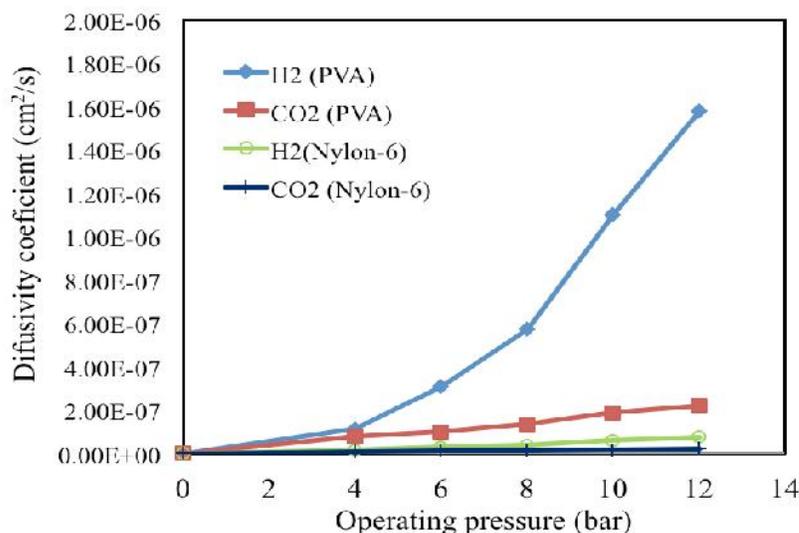

Fig.7. Diffusivity of H_2 and CO_2 on PVA and Nylon-6 at various feed operating pressures.

Comparing the ideal selectivity of pure gas permeation, the slectivity of Nylon-6 at the highest operating pressure was about 4.9 that is two times higher than that of PVA membrane as shown in Fig.10.
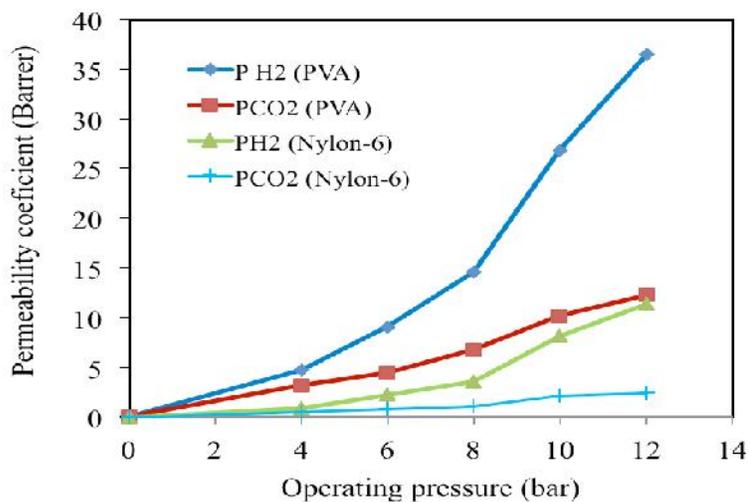

Fig.8. Permeability of H_2 and CO_2 on PVA and Nylon-6 at various feed operating pressures
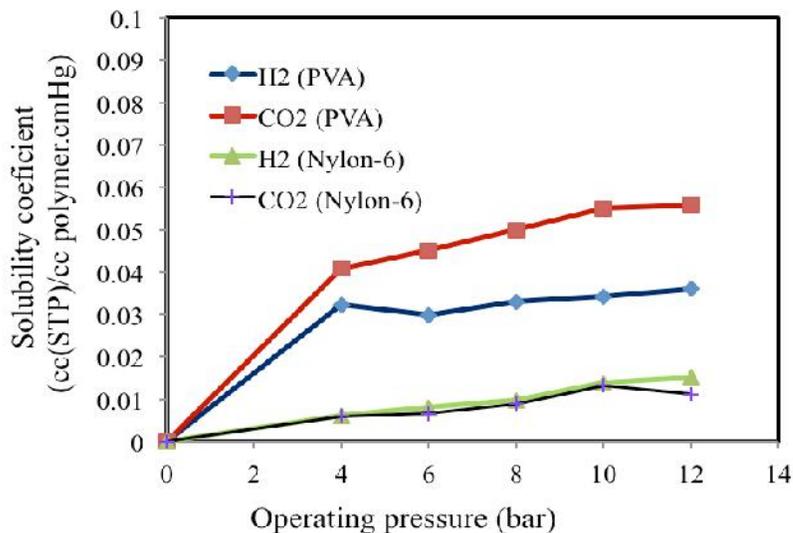

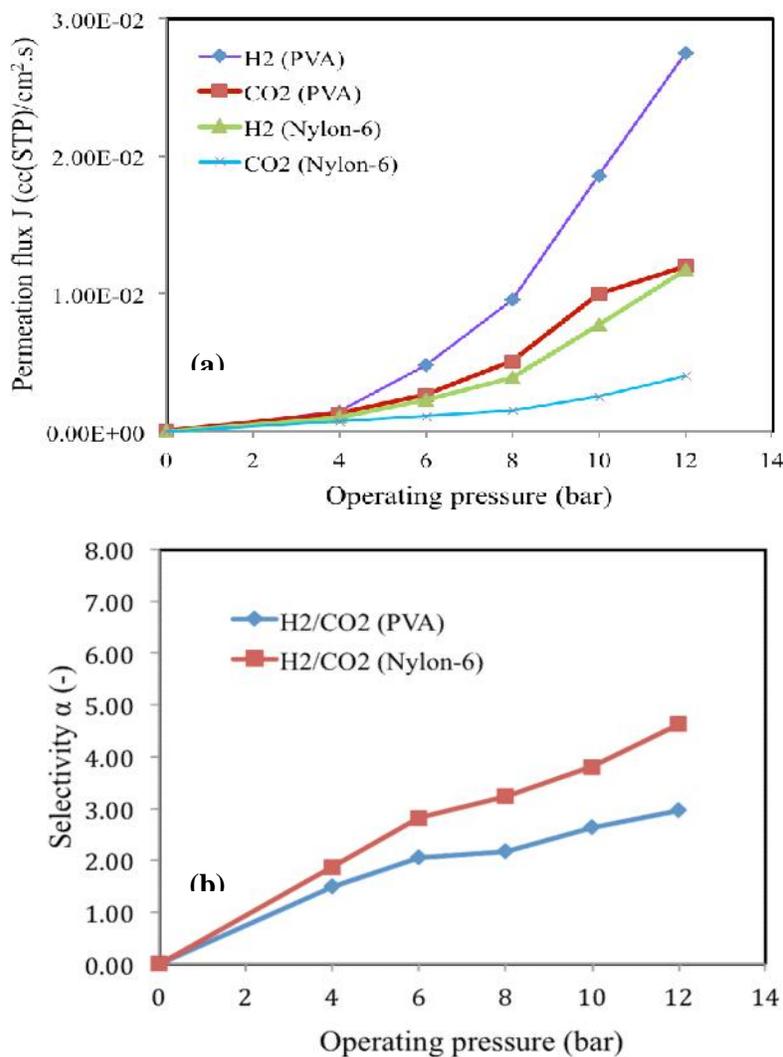Fig.9. Solubiliy of H_2 and CO_2 on PVA and Nylon-6 at various feed operating pressures.

Fig.10. Membrane performance on pure gas permeation. (a) Permeation flux (J) and (b) Selectivity of H_2/CO_2

4.2. Permeate Flux and Real Selectivity ( ) of mixed gas permeation

Figure 11 shows the experimental results of mixed gas. The flux increases with increasing the feed pressure, whereas selectivity decreases with increasing the feed pressure. These phenomena took place due to a couple effects interaction among molecules gas of H_2, CO_2 and membrane. Therefore, the gas molecules of CO_2 and H_2 will diffuse simultaneously. We can compare that the real selectivity

of PA membrane at 12 bar is about 3.78 and slightly higher than PVA membrane about 2.3. This because PA (Nylon-6) membrane have a rigid structure and smaller free void volume. Thus, when the feed pressure increase, the polymer matrix of PA (Nylon-6) became more compacted, which could lowered gas diffusion through membrane.
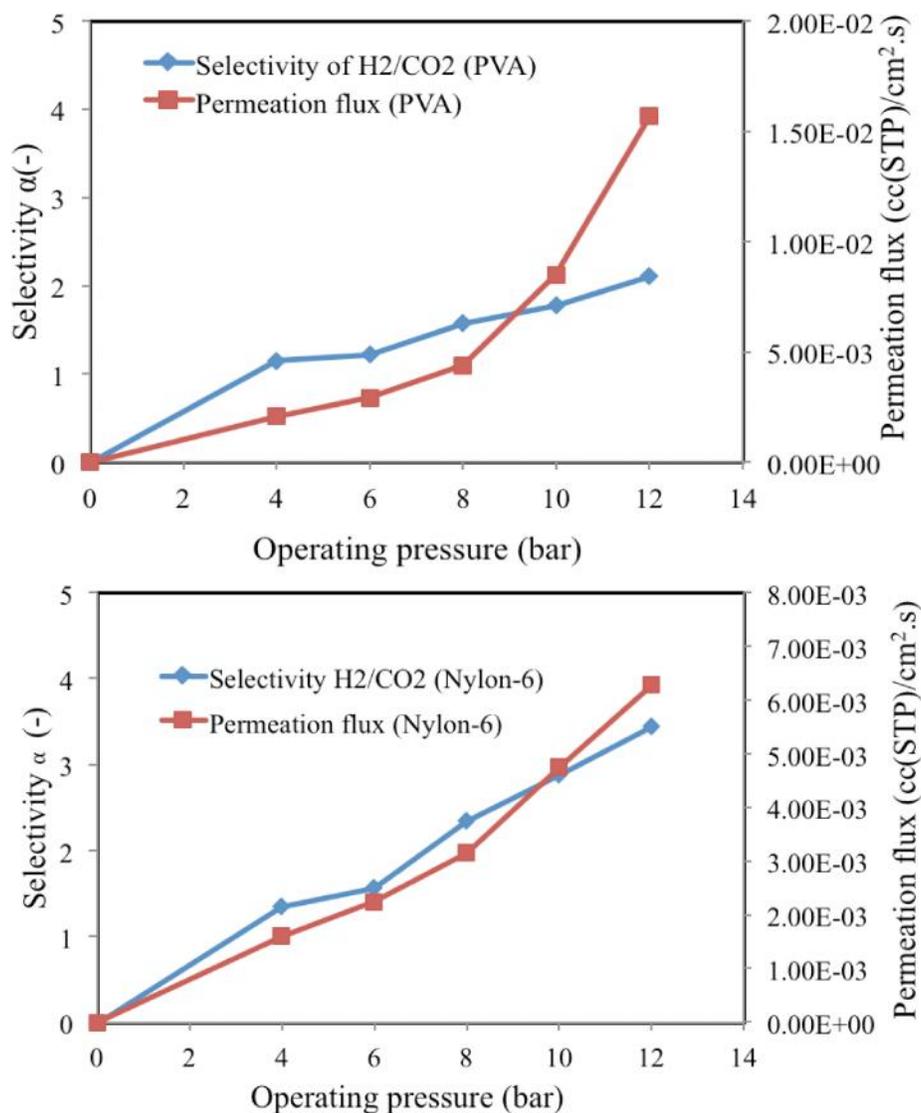

Fig.11. Membrane performance on mixed gas permeation. (a) PVA membrane and (b) Nylon-6 membrane

5. Conclussion

From the experimental results, it can be concluded that solubility coefficient of CO_2 in PVA membrane was greater than in PA (Nylon-6) membrane, and decreased for increasing pressure. Permeability coefficient and permeate flux of H_2 were higher at both two types of membranes. The selectivity of H_2/CO_2 by using PA (Nylon-6) membrane was higher both at pure permeation and at mixture gas permeation compared to PVA membrane. For further experiment, it is suggested to study about behavior of the actual mass transport of molecule gas thorough membrane and to consider the effect of dual sorption and dual diffusion on the gas separation.

6. References

1. Brunetti, A., F. Scura, G. Barbieri, E. Drioli (2010), Membrane technologies for CO2 separation, *Journal of Membrane Science*, **359** 115–125.

2. Feng, X., P. Shao, R.M.Y, Huang., G. Jiang., R.X. Xu (2002), A study of silicone rubber/polysulfone composite membranes: correlating H2/N2 and O2/N2 permselectivities, *Separation and Purification Technology*, **27**, 211–223.

3. Gu, Y., E. L. Cusller, T.P. Lodge (2012), ABA-triblock copolymer ion gels for CO2 separation applications, *Journal of Membrane Science*, **423-424**, 20–26.

4. Kim, H.W., H. B. Park (2011), Gas diffusivity, solubility and permeability in polysulfone–poly (ethylene oxide) random copolymer membranes, *Journal of Membrane Science*, **372,** 116–124.

5. Li, P., T.S. Chung, D.R. Paul (2013), Gas sorption and permeation in PIM-1, *Journal of Membrane Science*, **432**, 50–57.

6. Morisato, A., Z. He, I. Pinnau (1999), Mixed-Gas Permeation Properties and Physical Aging of Poly(4-methyl-2-pentyne): in Polymer Membranes for Gas and Vapor Separation (Chemistry and Materials Science) Freeman, B. D and Pinnau, I. Editors, *ACS Symposium Series*,**733**, American Chemical Society, Washington, DC (1999), 57–67.

7. Shao, L., B. T. Low, T. S. Chung, A.R. Greenberg (2009), Polymeric membranes for the hydrogen economy: Contemporary approaches and prospects for the future, *Journal of Membrane Science*, **327**, 18–31.

8. Thomas, S., I. Pinnau, N. Dub, M. D. Guiver (2009), Pure- and mixed-gas permeation properties of a microporous spirobisindane-based ladder polymer (PIM-1), *Journal of Membrane Science*, **333**, 125–131.

9. Zhao, L., E. Riensche, R. Menzer, L. Blum, D. Stolten (2008) A parametric study of CO2/N2 gas separation membrane processes for post-combustion capture, *Journal of Membrane Science*, **325**, 284–294.

10. Wijmans, J.G., R.W. Baker (1995), The solution-diffusion model: a review, *Journal of Membrane Science*, **107**, 1-21.