



# Separation of carbon dioxide (CO<sub>2</sub>) from gas mixture by membrane permeation process

V. Soesilowati Praptowidodo

Membrane and Polymer Technology Laboratory; Department of Chemical Engineering ITB  
e-mail: vsp@che.itb.ac.id; Telp:(022)2500989; Fax: (022)2501438

Masuk: ; revisi masuk: ; diterima:

## Abstract

Removal of CO<sub>2</sub> from natural gas and combustion exhaust gas have been studied by employing membrane permeation process. In these studies, polysulfone, polyimide and polydimethylsiloxane membranes are used to elucidate the influence of flexibility and rigidity of polymer as well as the influence of polar groups within polymer matrix on gas transport through membrane. The performance of the membranes as specified by its selectivity and permeation flux are measured in terms of the diffusion and sorption coefficients as well as the permeability. It is found that flexibility of the membrane tends to suppress its selectivity while enhancing its permeation flux. On the other hand, rigidity of the membrane together with the polar groups is shown to induce the opposite effects. In both cases however, the selectivity and permeation follow approximately the same qualitative variations with respect to concentration which is suspected to be caused by the plasticization effect in the membrane. It is therefore concluded that a rigid polymer membrane with polar groups is most effective for its performance.

*Key words:* membrane; polymer; polar; permeation; separation; selectivity.

## Sari

### Pemisahan karbon dioksida (CO<sub>2</sub>) dari campuran gas dengan permeasi membran

Penghilangan CO<sub>2</sub> dari gas alam dan gas buang hasil pembakaran dipelajari dengan cara permeasi membran. Dalam studi ini membran polisulfon, polimid, dan membran karet silikon (polidimetilsilosan) dipergunakan dalam rangka mempelajari pengaruh kelenturan dan kekakuan polimer serta pengaruh gugus polar dalam matriks polimer pada perpindahan gas melalui membran. Kinerja membran ditentukan oleh selektivitas dan fluks permeasi yang diukur dari besaran koefisien difusi, koefisien sorpsi dan permeabilitas. Hasil percobaan menunjukkan bahwa kelenturan membran cenderung menekan selektivitas namun dapat menaikkan fluks permeasi. Sedangkan kekakuan membran disertai gugus polar dalam matriks polimer memberikan efek yang berlawanan. Dalam kedua kasus tersebut, selektivitas dan fluks permeasi mengikuti variasi kualitatif yang mirip terhadap pengaruh konsentrasi CO<sub>2</sub>, diperkirakan dapat menyebabkan efek plastisasi dalam membran. Didasarkan pada hasil penemuan seperti tersebut di atas, maka dapat disimpulkan bahwa polimer membran kaku dengan gugus polar merupakan membran yang paling efektif untuk penghilangan CO<sub>2</sub> dari gas alam dan gas buang hasil pembakaran.

*Kata kunci :* membran; polimer; polaritas; pemisahan; permeasi; selektivitas.

## 1 Introduction

Membranes application to separation process is recently expanding in many industries [1]. Several gas separation processes by means of membrane are employed to produce high purity gas or to remove some undesirable contaminants, such as that contained in natural gas CO<sub>2</sub> content extending from 2 to 70%. The removal of CO<sub>2</sub> is necessarily since CO<sub>2</sub> will be frozen at a low refrigeration temperature and accordingly will plug in the piping system in a LNG processing plant.

Nowadays the environmental aspect of global warming due to high emission of CO<sub>2</sub> from exhaust gas has also become an important global issue. Technology is being developed to concentrate CO<sub>2</sub> from exhaust gas to be processed further for C-1 chemistry [2]. Gas separation research on CO<sub>2</sub> removal is currently still being

conducted by way of developing a membrane that has the specific high selectivity and high permeability. A thorough and better understanding of transport phenomena through a membrane, by exploring all of the influencing factors is therefore required in order to develop permselective membrane in a gas separation process [3,4].

In this paper the result of a study on the gas transport mechanism through membranes of different structure and polymeric materials at various feed gas pressures for a number of gas compositions is reported. The effects of those factors in the gas transport mechanism will also be shown in this study.

## 2 Theory

Polymeric materials at glassy state are rigid glasslike, while at rubbery state they are flexible rubberlike. Glass transition temperature  $T_g$  of a polymer is the transition temperature at which polymer will undergo a change of state, i.e. from a glassy to a rubbery state. The state of polymer undoubtedly will take an important factor in gas separation that employs a nonporous polymeric membrane [5]. At glassy state free volume is found relatively constant in amount while at rubbery state it will increase according to the following relation:

$$v_f = v_{f,T_g} - \Delta\alpha(T - T_g) \quad (1)$$

Where  $v_f$  is free volume at temperature  $T$  above  $T_g$ ,  $v_{f,T_g}$  is free volume at  $T$  below  $T_g$  and  $\Delta\alpha$  is the thermal expansion coefficient.

The concept of free volumes will be helpful to illustrate gas transport phenomena through a nonporous membrane. Microscopically free volume is an empty space that is found in between polymer chains; besides this free volume however, polarity of chemical groups will also yield an interaction between gas penetrant and membrane [5].

### 2.1 Transport phenomena through a nonporous membrane

Transport mechanism of gases through a nonporous dense polymeric membrane can be described by way of the solution-diffusion mechanism. Sorption phenomena of a gas into membrane are determined by the nature of interaction that exists between gas and the corresponding membrane. The higher critical gas temperature  $T_c$ , gas will be more condensable and soluble and gas polarity will also promote the interaction to polar membrane. The sorption isotherm of gases within membrane will follow either Henry's law, or Langmuir, and dual mode sorption model. Diffusion of gases into membrane is random movements of gas molecules within membrane that start at the upstream toward downstream sides of membrane. Within a homogeneous dense membrane, the diffusion equation can be derived from Fick's first law:

$$J = D \frac{C_1 - C_2}{l} \quad (2)$$

Where  $J$  is the volumetric flux in  $cc(STP)/cm^2.s$ ,  $D$  diffusion coefficient in  $cm^2/sec$ ,  $C$  represents gas concentration within membrane and  $l$  is membrane thickness. Subscript 1 and 2 refers, respectively, to upstream and downstream sides of membrane.

Assuming Henry's law  $C = S x p$  where  $S$  is the sorption coefficient and  $p$  the feed gas pressure, and substituted this expression into equation (2) for each of the  $i$ -th component in the mixture yields:

$$J_i = D_i S_i \frac{(p_{i1} - p_{i2})}{l} \quad (3)$$

According to Solution - Diffusion mechanism  $P_i = D_i S_i$ , then substituted to (3) thus

$$J_i = P_i \frac{(p_{i1} - p_{i2})}{l} \quad (4)$$

where permeability coefficient  $P_i$  for each component is expressed in Barrer.

$$1 \text{ Barrer} \approx 10^{-10} \text{ cm}^3(\text{STP})(\text{cm.sec})^1 \cdot \text{cmHg}^{-1} [5].$$

### 2.2 Determination of transport parameters $P$ , $D$ and $S$

Diffusion coefficient  $D$  and permeability coefficient  $P$  each is determined by means of the Time Lag method. From steady state volumetric flow rate of permeate gas curve  $Q_t$  vs time  $t$ , the intersection between straight line with the X-axis represents time lag  $\theta$ . The general relation of permeation curve is given by

$$\frac{Q_t}{l c_i} = \frac{D t}{l^2} - \frac{1}{6} - \frac{2}{\pi} \sum_{n=1}^{\infty} \left( \frac{(-1)^n}{n^2} \right) \exp \left( \frac{-D n^2 \pi^2 t}{l^2} \right) \quad (5)$$

which for  $t \approx \infty$  yields

$$Q_t = \frac{D c_i}{l} \left( t - \frac{l^2}{6D} \right) \quad (6)$$

Then

$$\frac{V}{A p_i} = \frac{P}{l} t - \frac{P}{6D} l \quad (7)$$

Thus

$$D = \frac{l^2}{6\theta} \quad (8)$$

Equation (8) will yield diffusion coefficient  $D$  while permeability coefficient is determined from the slope of the corresponding curve.

### 2.3 Separation factor

In industrial applications, the high permeability as well as high selectivity membrane, is required to separate gas. The selectivity can be examined from the ideal one that is represented by the ratio of permeability coefficients of pure gases, i.e.:

$$\alpha_{ideal} = P_A / P_B \quad (9)$$

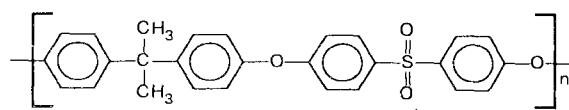
For a gas mixture it is determined by the ratio of gas composition within the permeate in feed streams as permeation process occurs, that is

$$\alpha = \frac{y_A / y_B}{x_A / x_B} \quad (10)$$

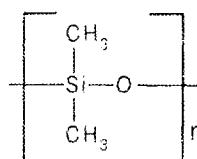
where  $y_A$  and  $y_B$  is mole fraction of gas  $A$  and  $B$ , respectively, within the permeate and  $x_A$  and  $x_B$  is mole fraction of gases in feed stream.

### 3 Materials and method

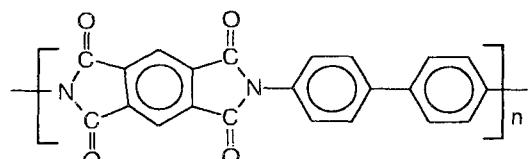
In this study, polydimethylsiloxane ( $T_g = -123^\circ\text{C}$ ), polysulfone ( $T_g = 195^\circ\text{C}$ ) and polyimide ( $T_g = 315^\circ\text{C}$ ) have been employed. Polysulfone and polyimide membrane have been prepared by phase inversion method; the composite membrane Polydimethylsiloxane (PDMS) has been prepared by way of coating a thin skin layer of PDMS gel upon porous polysulfone support [6]. The polymer structure of PDMS, Polysulfone and Polyimide are shown below



Polysulfone ( $T_g = 195^\circ\text{C}$ )



Polydimethyl siloxane  
( $T_g = -123^\circ\text{C}$ )



Polyimide ( $T_g = 315^\circ\text{C}$ )

Gas permeation was done by employing pure gases  $\text{CO}_2$ ,  $\text{CH}_4$ , a mixture of  $\text{CO}_2/\text{CH}_4$  as well as natural gas that have been provided by Pertamina LPG Refinery Plant at Mundu West Java. For exhaust gas mixture, in particular, gas permeation was carried out by pure gas  $\text{CO}_2$ ,  $\text{N}_2$ , and simulated by mixture of  $\text{CO}_2/\text{N}_2$ . The mixture was prepared by mixing pure  $\text{CO}_2$  with pure  $\text{N}_2$ , and the  $\text{CO}_2$  composition within mixture was varied from 10 to 35% by volume.

The operating condition for (following the  $\text{CO}_2$  concentration in combustion exhaust gas) permeation process was at room temperature and the pressure was varied from 2 - 10 bars. Bubble flow meter was applied to measure the permeate gas flow rate, and the corresponding transport parameters can be found by means of the relation between gas volumetric flow rate to permeation time, as the process has been in steady state. The respective value of diffusion coefficient  $D$ , permeability coefficient  $P$ , and solubility coefficient  $S$ , each can be found from the available experimental permeation data. Membrane performance is determined by measuring per

meation flux; separation factor (selectivity  $\alpha$ ) can be calculated from the gas composition within feed stream and product gas. Gas composition was analyzed by means of gas chromatography (GC), and membrane structure by means of Scanning Electron Micrograph (SEM). The experimental set up is shown as Figure 1.

### 4 Results and discussion

#### 4.1 Membrane structure

Scanning Electron Micrograph (SEM) has been applied to observe the structure of PDMS membrane as shown as Figure 2. The structure consists of a homogeneous, dense and nonporous layer. Similarly the observed structure of polysulfone membrane is asymmetric in nature as shown

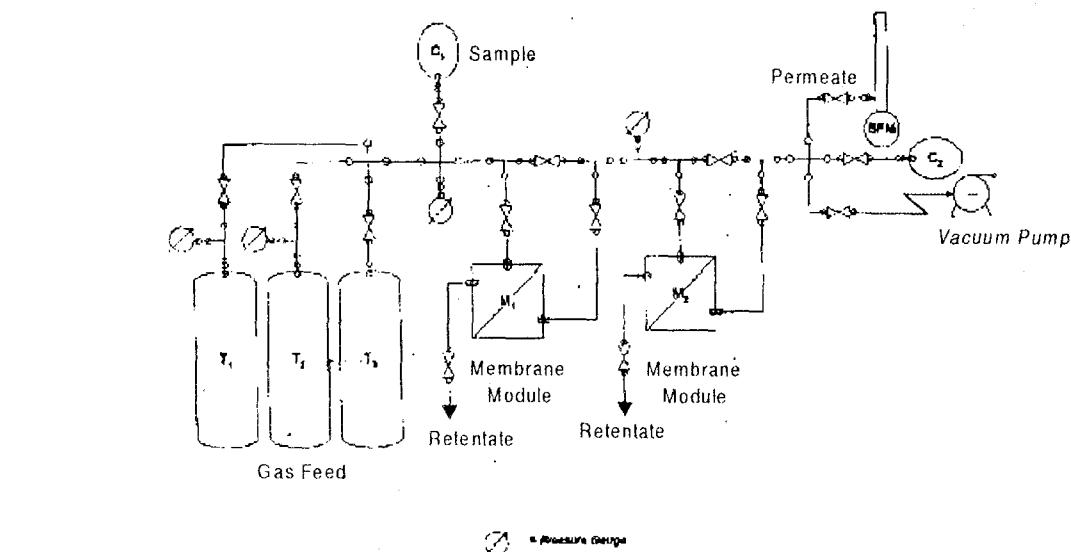


Figure 1 Gas permeation equipment

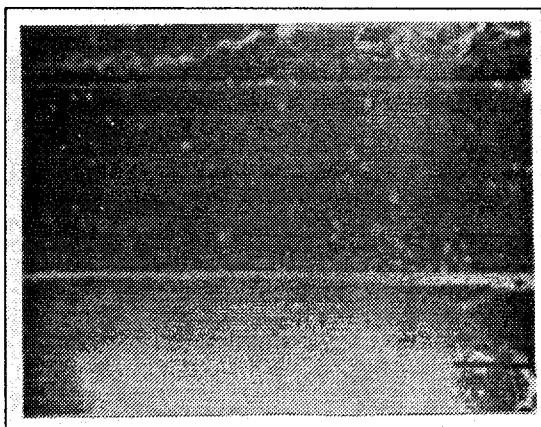


Figure 2 SEM of PDMS membrane

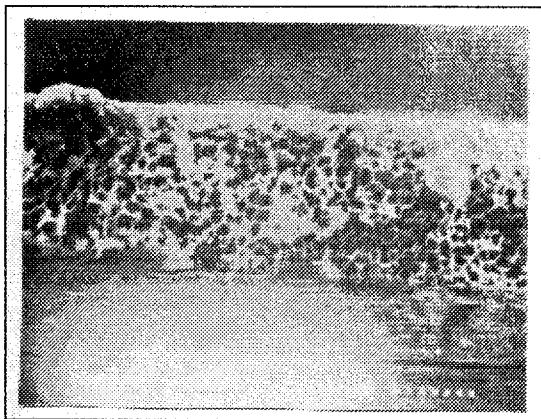


Figure 3 SEM of asymmetric polysulfone membrane

by figure 3. It is seen that the top layer is a thin and nonporous dense skin layer and it functions as an active layer in the gas separation process. The layer below this skin displays visible porous structure. In other word, both membrane share similar structures characterized by a nonporous dense skin layer supported by a much thicker porous layer. As a dense membrane, each of them is thus expected to follow the solution-diffusion mechanism in their gas transportation processes.

## 4.2 Gas permeation

### 4.2.1 Pure gas $\text{CO}_2$ and $\text{CH}_4$

Transport Parameters i.e., Diffusion (D), solubility (S) and Permeability (P) coefficients of  $\text{CO}_2$  and  $\text{CH}_4$  in PDMS and Polysulfone membranes are given in Table 1 and Table 2, as well as the selectivity /separation factor ( $\alpha_{\text{CO}_2/\text{CH}_4}$ ) of pure gases in PDMS and polysulfone membranes.

From Table 1, the diffusion coefficient of  $\text{CO}_2$  in PDMS membrane decreases with the increase of feed gas pressure from 2 to 8 bars, on the other hand solubility coefficient increases. Permeability coefficient is relatively constant because  $P = D \times S$ .

The diffusion coefficient of  $\text{CH}_4$  in PDMS membrane also decreases with the increase of feed gas pressure. The same variation is also found for the solubility coefficient of  $\text{CH}_4$  in PDMS membrane. The selectivity expressed by  $P_{\text{CO}_2}/P_{\text{CH}_4}$  in PDMS membrane is low and remains constant upon increasing feed gas pressure.

Table 1 Transport parameter and  $\alpha_{\text{CO}_2/\text{CH}_4}$  in PDMS membrane

Pressure (bar)	$\text{CO}_2$			$\text{CH}_4$			$\alpha_{\text{CO}_2/\text{CH}_4}$ ( $P_{\text{CO}_2} / P_{\text{CH}_4}$ )
	$D \times 10^8$ $\text{cm}^2/\text{s}$	P Barrier	S (=P/D) $\times 10^2$ CcSTP/ cc.cmHg	$D \times 10^8$ $\text{cm}^2/\text{s}$	P Barrier	S (=P/D) $\times 10^2$ CcSTP/ cc.cmHg	
2.0	12800	3840	0.30	12900	1161	0.09	3.31
3.5	7090	4112	0.58	1800	1278	0.71	3.22
5.0	1820	3986	2.19	904	1238	1.37	3.22
6.5	1340	4074	3.04	733	1165	1.59	3.50
8.0	1250	3950	3.16	646	1227	1.9	3.22

Table 2 Transport parameter of  $\text{CO}_2$  and  $\text{CH}_4$  in polysulfone membrane

Pressure (bar)	$\text{CO}_2$			$\text{CH}_4$			$\alpha_{\text{CO}_2/\text{CH}_4}$ ( $P_{\text{CO}_2} / P_{\text{CH}_4}$ )
	$D \times 10^8$ $\text{cm}^2/\text{s}$	P Barrier	S (=P/D) $\times 10^2$ CcSTP/ cc.cmHg	$D \times 10^8$ $\text{cm}^2/\text{s}$	P Barrier	S (=P/D) $\times 10^2$ CcSTP/ cc.cmHg	
2.0	6.76	89.93	13.30	1.42	5.27	3.71	17.06
3.5	10.70	99.76	9.32	1.87	5.06	2.71	19.72
5.0	14.30	103.40	7.23	3.22	5.08	1.58	20.35
6.5	29.40	105.19	3.58	4.69	4.95	1.06	21.25
8.0	105.00	102.44	0.98	5.33	4.33	0.81	23.66

Table 2 shows that the diffusion coefficients of  $\text{CO}_2$  and  $\text{CH}_4$  in polysulfone membrane are increase, while solubility coefficient of  $\text{CO}_2$  and  $\text{CH}_4$  decrease with operating pressure. The permeability coefficient of  $\text{CO}_2$  in polysulfone membrane increases with increasing feed gas pressure, it remains approximately constant for  $\text{CH}_4$ . We also note that the selectivity in Polysulfone membrane is higher than that of the PDMS membrane and it increases upon increase of feed gas pressure.

Comparison of Table 1 with Table 2 shows that Polysulfone membrane performs better for separation of  $\text{CO}_2/\text{CH}_4$  than PDMS membrane. At room temperature PDMS is a rubbery polymer while Polysulfone is glassy polymer; gas diffusion through a flexible membrane is faster than through a rigid glassy membrane. In such a case all gases will permeate easily through PDMS without separation. Diffusion within a rigid polysulfone membrane will happen through the holes of free volumes that exist within membrane matrix, and the selective transport will be promoted by the interaction developed between polar  $\text{CO}_2$  gas with the polar group in membrane matrix. Therefore separation of  $\text{CO}_2/\text{CH}_4$  by polysulfone membrane is expected to be more effect than in PDMS membrane.

#### 4.2.2 Gas mixture of $\text{CO}_2$ and $\text{CH}_4$

Gas permeation of  $\text{CO}_2/\text{CH}_4$  mixture at constant pressure 8 bar and variation of  $\text{CO}_2$  concentration is shown by Figure 4 for PDMS membrane and Figure 5 for Polysulfone membrane. Figure 4 and Figure 5 depict the curve of selectivity and permeation flux upon concentration of  $\text{CO}_2$  from 20% to 80% in feed gas. The feed gas pressure is kept constant at 8 bar. In both figures the permeation flux increases by the increase of  $\text{CO}_2$  concentration, while selectivity decreases slightly and almost constant at  $\text{CO}_2$  concentration between 40 to 80%. PDMS membrane produces higher flux but lower selectivity to compare with polysulfone membrane. It is expected that flexibility of rubbery PDMS membrane promote high permeation rate, while in rigid polysulfone membrane the permeation rate is lower. High permeation rate of both  $\text{CO}_2$  and  $\text{CH}_4$  will result in low selectivity of PDMS membrane. The presence of polar groups in polysulfone on the other hand produces high selectivity (separation factor) for  $\text{CO}_2$  transport. By increasing concentration of  $\text{CO}_2$  from 20 to 80%, the permeation flux increases almost 4 times in polysulfone membrane and selectivity decreases from 12 to 8 (Figure 5). Increasing flux mean that larger free volume is developed in the membrane matrix; due to effect of plasticization caused by the interaction of large amount of  $\text{CO}_2$  with the polar groups in the membrane matrix.

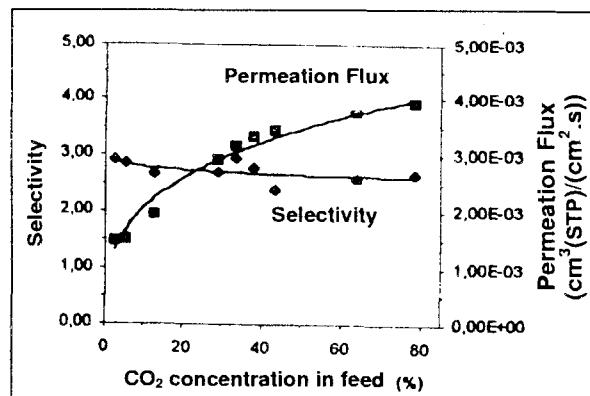


Figure 4 Selectivity and Permeation flux vs  $\text{CO}_2$  concentration in PDMS Membrane (Operating Pressure 8 bar)

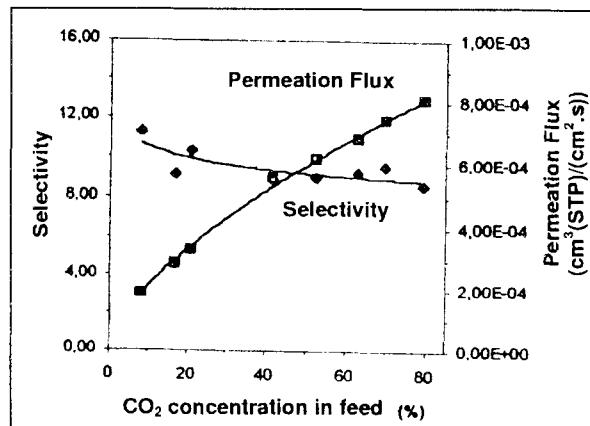


Figure 5 Selectivity and Permeation flux vs  $\text{CO}_2$  concentration in Membrane Polysulfone (Operating Pressure 8 bar)

#### 4.2.3 Removal of $\text{CO}_2$ from natural gas

Natural gas that has been provided by LPG plant Pertamina at Mundu contains 2.4%  $\text{CO}_2$  by volume and some contaminants such as ethane, propane and butane. Performances of gas permeation through PDMS and polysulfone membrane are presented as Figure 6 and Figure 7, respectively. As shows in the figures, the permeation flux increases with increasing feed pressure. Selectivity in PDMS is almost constant irrespective of variation of feed gas pressure. However, it increases with pressure in polysulfone membrane. Looking at Table 3 and Table 4, the selectivity ranges from 2.28 to 2.92 for PDMS, and from 5.51 to 10.06 for polysulfone, corresponding to feed gas pressure from 3 to 8 bars. In this respect, feed gas pressure influences the selectivity of polysulfone membrane but not that of PDMS membrane. Approximately the polar interaction effected by increasing pressure promotes the flux and selectivity of  $\text{CO}_2$  from natural gas in polysulfone membrane.

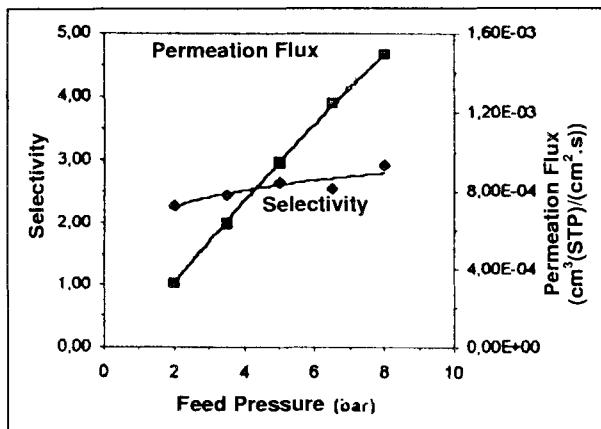


Figure 6 Selectivity and Permeation flux of Natural Gas in PDMS Membrane

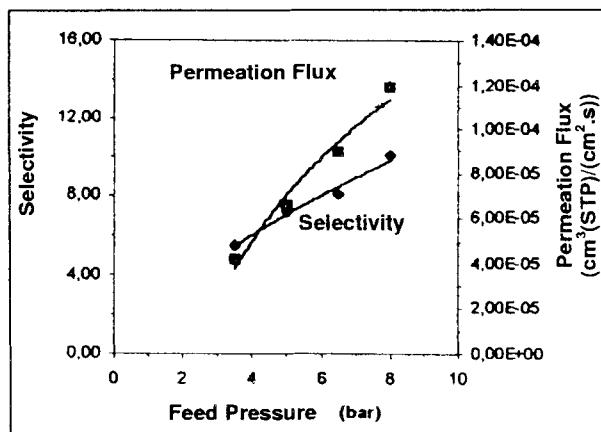


Figure 7 Selectivity and Permeation flux of Natural Gas in Membrane Polysulfone

Table 3 Selectivity and Permeation flux of Natural Gas in PDMS Membrane

No	Feed Pressure	Permeate Composition Weight %		Retentate Composition Weight %		$\alpha$	Permeation flux (cm³ (STP)/s)
		CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>		
1	2.0	3.83	96.17	1.72	98.28	2.28	3.32E-04
2	3.5	4.59	95.41	1.92	98.08	2.46	6.43E-04
3	5.0	4.87	95.13	1.90	98.10	2.64	9.54E-04
4	6.5	4.87	95.13	1.97	98.03	2.55	1.24E-03
5	8.0	5.10	94.90	1.81	98.19	2.92	1.49E-03

Table 4 Selectivity and Permeation flux of Natural Gas in Membrane Polysulfone

No	Feed Pressure	Permeate Composition Weight %		Retentate Composition Weight %		$\alpha$	Permeation flux (cm³ (STP)/s)
		CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>		
1	3.5	11.70	88.30	2.35	97.65	5.51	4.17E-05
2	5.0	13.52	86.48	2.13	97.87	7.18	6.56E-05
3	6.5	14.50	85.50	2.06	97.94	8.06	8.95E-05
4	8.0	14.13	85.87	1.61	98.39	10.06	1.19E-04

From Table 4 it is remarkable that CO<sub>2</sub> in natural gas decrease to 1.61 %.

#### 4.2.4 Pure gas CO<sub>2</sub> and N<sub>2</sub>

The result of gas permeation of pure CO<sub>2</sub> and N<sub>2</sub> in PDMS and polyimide membrane are shown by Figure 8. The selectivity of each of the membranes in variation of feed gas pressure from 2 to 10 bar increases by the increase of feed gas pressure. Polyimide membrane possesses higher selectivity than PDMS. It can be explained that free volume in rigid Polyimide and the existence of polar groups are expected to promote the selective transport of CO<sub>2</sub> through the membrane that is shown by Figure 9.

#### 4.2.5 Permeation of gas mixture CO<sub>2</sub>/N<sub>2</sub> in polyimide membrane

Polyimide membrane has been chosen in the separation of CO<sub>2</sub>/N<sub>2</sub> mixture at room temperature and at pressure 10 bar; CO<sub>2</sub> concentration in the mixture is within the range of 10 to 35% by volume. The variation of composition CO<sub>2</sub> is approaching the composition of combustion exhaust gas mixture. The increased concentration of CO<sub>2</sub> in the mixture will result a slight change to membrane structure as is shown by Figure 9. Increasing the CO<sub>2</sub> concentration in gas mixture will result in decreasing the selectivity. Plasticization is predicted to occur due to the interaction between membrane and CO<sub>2</sub> at high concentration and accordingly it will reduce the strength of secondary bond that is found in between polymer chains, thus free volume will be increased, and in return it will allow permeation to both of CO<sub>2</sub> and N<sub>2</sub>.

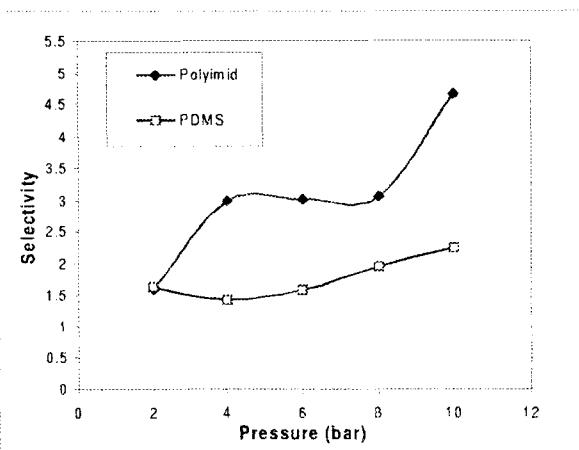


Figure 8 Ideal selectivity versus feed pressure for polyimide and PDMS membrane

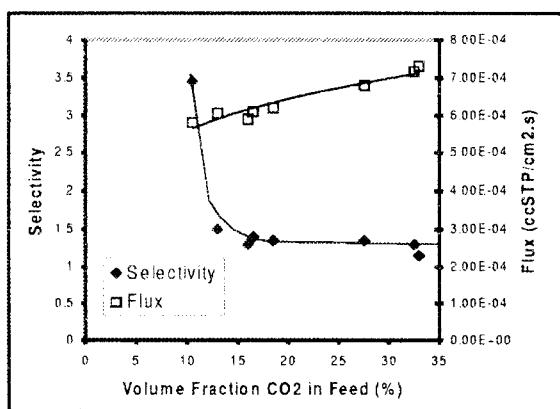


Figure 9 Selectivity and flux permeate versus CO<sub>2</sub> concentration for polyimide membrane (Operating Pressure 8 bar)

## 5 Conclusion

Based on the results discussed above we arrive at the following conclusions.

In the case of pure gas, the selectivity ( $P_{CO_2}/P_{CH_4}$ ) of flexible PDMS membrane appears almost unaffected by increasing feed pressure of the gas, while it clearly increases for the rigid and polar polysulfone membrane. In the case of mixed gas, the feed gas pressure generally increases the permeation flux, and to a lesser degree the selectivity as well, although the increase of selectivity is more significant for the polysulfone membrane. This gas pressure induced increases are likely due to plasticization effect caused by interaction between the membrane and CO<sub>2</sub>. For the separation of CO<sub>2</sub>/N<sub>2</sub> in exhaust gas the selectivity of CO<sub>2</sub> in both PDMS and Polyimide membranes tends to increase with increasing gas pressure, with the latter showing much larger effect. This difference is supposed to have its origin in the polar nature of Polyimide membrane and the related plasticization effect. In all cases however, the plasticization effect tends to saturate at higher concentration of CO<sub>2</sub>.

In short, the separation of CO<sub>2</sub> from natural gas and combustion exhaust gas can be achieved most effectively

by developing a rigid membrane base on polymer with certain polar groups.

## 6 Acknowledgements

The author is grateful to Dr. M.O. Tjia for his critical reading and discussions of the manuscript. This research was supported by Osaka Gas Foundation 1998-1999.

## 7 References

1. Fouda, A.E., Hazlet, J.D., Matsuura, T. and Johnsons, J., editors, Membrane gas separation and design, *AIChE Symposium Series*, **85**, 41-80, (1989).
2. Bobcock, R.E., Spillman, R.W., Goddin, C.S. and Cooley, T.E., Natural gas cleanup: A comparison of membrane and amine treatment processes, *Energy Progress*, **8**, 135-142, 1988.
3. Hinchliffe, A.B., Targetting the development of membranes for gas separation, *J. Chem. Tech. Biotechnol.*, **62**, 211-221, 1995.
4. Lee, A.L., Feldkircher, H.L., Gamez, J.P. and Meyer, H.S., Membrane process for CO<sub>2</sub> removal tested at Texas Plant, *Oil & Gas Journal*, Jan., **31**, 90-91,
5. Mulder, M., Material and material properties, Transport in membrane, Gas separation in *Basic principles of membrane technology*, Kluwer Academic Publ., Dordrecht, 2<sup>nd</sup> ed., 17-52, 145-196, 220-233, 1996.
6. Kesting, R.E. Membrane separation processes, phase-inversion membrane in *Synthetic polymeric membrane*, John Wiley & Sons, New York, 22-78, 237-285, 1985.
7. Kazama, S., Sumiyama, Y., Matsuzaki, Y., Okabe, K., Mono, H., Haraya, K. and Kamizawa, C., Cardo polymer membrane for CO<sub>2</sub> separation, *Proceeding of international congress on membranes and membrane processes*, Heidelberg, Germany, 2.9, 1993.