The CO_2/CH_4 Separation by Commercially Available PPO and Cardo-type Polyimide Hollow Fiber Membranes

M. Pourafshari Chenar[a], M. Soltanieh[a,*], T. Matsuura[b], A. Tabe-Mohammadi[b,c]

[a] Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran
[b] Industrial Membrane Research Institute, Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada

10th Iranian Chemical Engineering Congress
Sistan & Balochestan University
15-17 November, 2005

[c] Present address: Ministry of the Environment, Environmental Sciences and Standards Division, 40 St. Clair Ave. West, Toronto, Ontario, Canada, M4V 1M2

Abstract

The CO_2/CH_4 and O_2/N_2 separations by commercially available PPO and Cardo-type polyimide hollow fiber membranes were investigated. Based on pure N_2, O_2, CH_4 and CO_2 permeation experiments, it was concluded that these hollow fiber membranes are good candidates for O_2/N_2 and CO_2/CH_4 separations. Gas mixture transport was determined by three different concentrations of CO_2 in CO_2-CH_4 gas mixtures (5%, 10% and 24.6% CO_2-balance CH_4) at room temperature and three different stage-cuts for each feed concentration. The feed side and permeate side pressures were 100 psig and atmospheric respectively. It was concluded that at stage-cuts proportional to feed CO_2 concentrations (Vol.%), the obtained separation factors were approximately equal.

Keywords: Commercial membranes, Gas separation, Stage-cut effects, Hollow fiber

1. Introduction

Although the concept of gas separation by membranes is more than 150 years old and the first publications were made by Mitchell and Graham [1, 2], large scale membrane applications remained limited until the main breakthrough in the formation of appropriate membranes with higher fluxes came with the development of asymmetric cellulose acetate membranes for reverse osmosis water desalination

---

[*] Corresponding author
E-mail address: msoltanieh@sharif.edu

by Loeb and Sourirajan [3]. These reverse osmosis membranes, when dried in a manner to preserve their porosity and the surface pore structure, showed higher permeation rates and significant separations for gaseous mixtures [4, 5].

In comparison with traditional gas separation technologies, membranes offer a number of advantages including: lower capital and operating costs, operational simplicity, good weight and space efficiency and flexibility of operation. On the other hand, membranes can not compete with the traditional technologies on the basis of product purity. Membranes can be used in combination with traditional gas separation processes to take advantages of both processes that neither process could achieve individually. For example, in the case of natural gas sweetening, the bulk CO_2 can be separated with membranes and the final purification to pipeline quality gas can be performed by an amine absorption process, or for available amine plants, a capacity increase can be achieved by integrating a membrane unit.

The selection of a membrane for such practical use is essentially based on gas permeation properties, permselectivity, mechanical strength and long-term durability of the membrane. Unfortunately, most membranes that have high permeability for gases usually have low to moderate selectivity. On the other hand, highly selective membranes are not very permeable. This trade-off relationship was demonstrated by Robeson’s upper bound lines [6, 7].

Among the glassy polymers, polyimides and PPO (also mentioned in the literatures as polyphenylene ether [8]) possess excellent separation properties and have received more attention for gas separations. It was reported that these two polymers were located close to Robeson’s trade-off line and even had better performance than the upper bound line [9, 10].

Polyimides seem to be good candidates for use as gas separation membrane materials, because of their high permselectivity in comparison with other membranes made from conventional glassy polymers, especially for the CO_2/CH_4 separation.

Polyimide hollow fiber membranes that were developed for CO_2/N_2 separation by “Research Institute of Innovative Technology for the Earth” (RITE, Japan), showed higher CO_2/N_2 permselectivity than commercially available hollow fiber membranes and had excellent properties for practical use such as [11]:

1) Excellent gas permselectivity and good permeability;
2) Easy fabrication (excellent solubility in organic solvents); and
3) Excellent thermal stability.

The high CO_2/N_2 selectivity of these Cardo-type polyimides is related to their high CO_2 solubility compared to conventional polymers. On the other hand, the gas diffusivity of these polymers is nearly equal to that of the commercial polymers [12].

There are many publications regarding the Cardo-type polyimide hollow fibers, and some modifications and improvements were made by RITE researchers on this type of polymides [11, 12, 13 and 14]. It should be noted that only CO_2/N_2 permselectivity data were published for these types of commercial polymers in these investigations.

Another polymer that has received some attention for commercialization for gas separation is PPO, which has a wide range of applications in different sectors of the industry.

Among the glassy polymers, PPO shows one of the highest permeabilities to gases. This high permeability is attributed to the absence of polar groups in the main chain of PPO [15]. PPO also possesses excellent mechanical and thermal properties. It has high impact strength. It is also stiff, hard and extremely tough [16].

It should be noted that in almost all of the reported studies, low molecular weight PPO was used, while it was reported by several authors that high molecular weight PPO membranes possess higher gas permeation properties than low molecular weight PPO membranes [10, 17].

Although many studies on gas transport through films of different polymeric materials are found in the literatures, only a limited number of data are available regarding the commercially available hollow fiber membranes. For example, all the published data for commercially available Cardo-type polyimide hollow fibers correspond to CO_2/N_2 separation and data on PPO membranes are in most cases focused on polymer modification targeting higher selectivity for O_2/N_2 mixture and there are almost no data for CO_2/CH_4 separation properties of commercially available PPO.

The present investigation was aimed at providing additional information on the CO_2/CH_4 and O_2/N_2 separation of these commercially available PPO membranes (from Aquilo, the Netherlands) and Cardo-type polyimide hollow fiber membranes (from RITE, Japan).

The objective of this work is to prove that these membranes available as membrane modules are useful in the CO_2/CH_4 separations, especially for the use in hybrid systems for natural gas sweetening, and for the capacity increase of available amine absorption plants.

2. Experimental

2.1. Materials and modules

The commercially available PPO hollow fibers were generously supplied by Aquilo Gas Separation B.V., the Netherlands (Parker Filtration and Separation B.V., Netherlands). The measured inside and outside diameters of hollow fibers were 370 and 520 μm respectively. The PPO modules were assembled by loading a bundle of 10 fibers in a shell and tube structure. The feed gas was introduced inside the fibers and permeate was collected on the shell side, although the dense layer of PPO hollow fibers was found on the outside.

The Cardo-type polyimide hollow fiber modules were generously supplied by RITE, Japan. The inside and outside diameters of fibers were 370 and 500 μm . The specifications of both types of these modules (RITE-A and PPO#1) that were used for most of the experiments are shown in Table 1.

Table 1. Modules and hollow fibers specifications

Module name and type	Hollow fiber parameters		Module specifications	
	Inside diameter (μm)	Outside diameter (μm)	Number of fibers	Permeation area (cm^2)
RITE-A (Cardo-type PI)	370	500	135	416
RITE-B (Cardo-type PI)	370	500	82	157
PPO#1	370	520	10	49
PPO#2	370	520	10	51
PPO#3	370	520	10	62

RITE-A and PPO#1 were used for most of the experiments. Other Cardo-type polyimide hollow fiber module (RITE-B) and other PPO hollow fiber modules (PPO#2 and PPO#3) were used only for reproducibility experiments.

This table also shows the specifications of other Cardo-type polyimide hollow fiber module (RITE-B) and other PPO hollow fiber modules (PPO#2 and PPO#3) that were used only for reproducibility experiments.

The ultra high purity CO_2, CH_4, N_2, O_2 and CO_2/CH_4 gas mixture (CO_2/5% - CH_4/95% (volume percent), CO_2/10% - CH_4/90% and CO_2/24.6%- balance CH_4) purchased from Praxair Distribution Inc., Canada were used as feed gases.

2.2. Gas permeation experiments

A constant pressure system was chosen for the permeation and separation experiments, both with single gases and gas mixtures, because operational conditions of the system are more like those of practical applications. The experimental set-up is described in Figure 1.

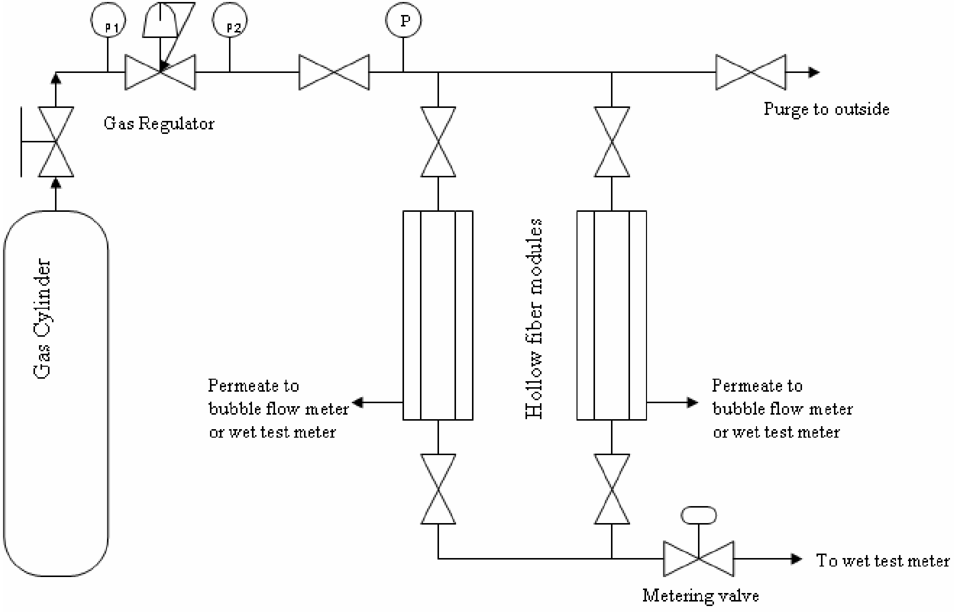

Fig. 1. Schematic diagram of the constant pressure testing system

The single gas permeation rates through hollow fiber membranes at room temperature were determined in a dead-end mode. Measurements were made at the feed stream pressures of 50, 75 and 100 psig, while the permeate side was kept at ambient pressures which were read from a barometer.

The pure gases were tested in the following order: N_2, O_2, and N_2 after O_2; CH_4, CO_2 and CH_4 after CO_2. The permeation rate was measured by a bubble-flow-meter when the flow rate was sufficiently low or by a wet-test-meter when the flow rate was high.

The permeance, defined as pressure-normalized flux of a membrane, is calculated from: $\frac{P}{\ell} = \frac{Q_P}{A\Delta p} \times 10^6 = \frac{F}{\Delta p} \times 10^6$ (1)

Where Q_P is the steady state permeation rate (cm^3 (STP)/s), F is the permeation flux, A is the permeation area of the membrane (cm^2) and Δp is the pressure gradient across the membrane (cm Hg).

Permeance calculated from Eq.1 has the unit of GPU, which is defined as:

$1\ GPU = 10^{-6}\ cm^3\ (STP) / (cm^2\ s\ cm\ Hg)$ (2)

The permeances obtained in single gas permeation tests were used to calculate the ideal selectivity (permselectivity) of gas A over gas B:

$$\alpha^{\circ}_{A/B} = \frac{(P/\ell)_A}{(P/\ell)_B} \tag{3}$$

After single gas permeation tests, the separation experiments of gas mixtures were conducted at the concentrations of CO_2 in CO_2/CH_4 gas mixtures mentioned earlier. The temperature was the ambient temperature and three different stage-cuts were employed for each feed concentration. The feed side and permeate side pressures were 100 psig and the ambient pressure, respectively.

The compositions of the retentate and permeate were determined by a gas chromatograph (Varian 3400) equipped with a thermal conductivity detector (TCD). The column of gas chromatograph was packed with "HayeSep Q".

The compositions of the permeate and retentate streams were determined by dividing the area under each peak by a specific thermal response factor (TRF). The details of the calculations are reported by Dietz [18]. The obtained TRF values for CO_2 and CH_4 were 48 and 36.2 respectively, which were in agreement with Dietz values of 48 and 35.7 [18]. The flow rate of the retentate gas was measured by a wet-test-meter and the permeate flow rate was measured by a bubble flow meter. The stage-cut was controlled by a metering valve which was attached to the retentate side and was calculated from:

$$\theta = \frac{Q_P}{Q_P + Q_R} \tag{4}$$

Where Q_P and Q_R are permeate and retentate flow rates respectively. Then $(P/\ell)_i$, and separation factor, α_{ij}, were determined by:

$$(\frac{P}{\ell})_i = \frac{Q_P y_i}{(p_f x_i - p_p y_i)A} \times 10^6 \tag{5}$$

$$\alpha_{ij} = \frac{y_i / x_i}{y_j / x_j} \tag{6}$$

Where y_i and x_i are the component mole fraction of permeate and feed gas respectively and p_f and p_p are feed and permeate side pressures.

Permselectivity was calculated for gas mixtures by Equation (3) based on the permeance data given by Equation 5.

3. Results and discussion

3.1. Cardo-type polyimide hollow fiber membranes

3.1.1. Pure gas permeation experiments

The test results of pure N_2, O_2, CH_4 and CO_2 gas permeation through Cardo-type polyimide hollow fibers at ambient temperature are shown in Table 2.

Permeation experiments with CH_4 were repeated after the experiments with CO_2. Similarly, N_2 experiments were repeated after O_2. The steady-state results and those values obtained immediately after the start of the experiment are compared in Table 2 with the values obtained before CO_2 and O_2 experiments, respectively.

Table 2. Permeances and Permselectivities of Cardo-type polyimide hollow fibers for gas pairs O2/N2 and CO2/CH4

Feed Pressure (Psig)	Permeance (GPU)						Permselectivity	
	N2	O2	N2 (after O2)	CH4	CO2	CH4 (after CO2)	CO2/CH4	O2/N2
50	2.82	15.8	2.84 (2.84)	2.60	89		34.1	5.6
75	2.97	17.1	3.11 (3.08)	2.84	101		35.7	5.8
100	3.14	18.0	3.28 (3.22)	2.90	111	2.73 (3.30)	38.1	5.7

The data in parenthesis are obtained immediately after the start of the experiments.

As expected, N_2 permeance after O_2 is slightly higher than that before O_2. On the other hand, CH_4 permeance after the CO_2 run was, quite unexpectedly, lower than the value obtained before the CO_2 runs. As it is seen in Figure 2, from the beginning of the experiment CH_4 permeance was higher than before CO_2 experiments. Then, CH_4 permeance became lower than before CO_2 experiments, gradually leveling off. This observation may be explained by plasticization effect of CO_2 especially at the beginning of the experiment.

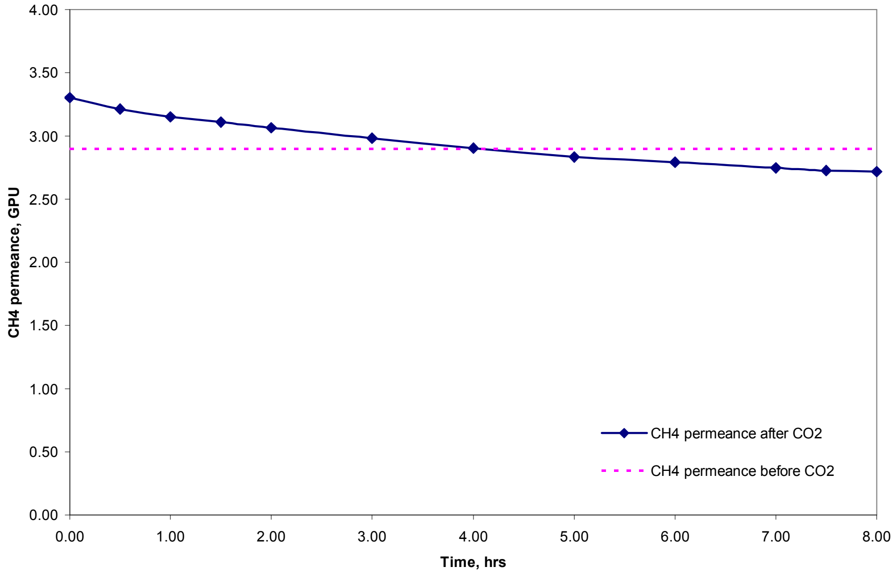

Fig. 2: CH_4 permeance before and after CO_2 permeation experiments. Module, Cardo-type polyimide module; feed pressure, 100 psig

This trend was completely reproducible since the same trend was also observed with another Cardo-type polyimide module (RITE-B). Most likely, CO_2 has plasticized the membrane. CH_4 permeance was high in the beginning because of the plasticization but decreased gradually as a result of compaction of the softened polymeric material.

Figure 3 shows the change in pure CO_2 permeance with time when the feed pressure was 100 psig. This decreasing trend was also observed earlier by Karashima et al. [11]. They assumed that the polymer structure has changed due to slow polymer relaxation.

It should be noted that a decrease in CH_4 permeance with time might have occurred even before the exposure of the membrane to CO_2. But the change was so small that a clear trend could not be observed.

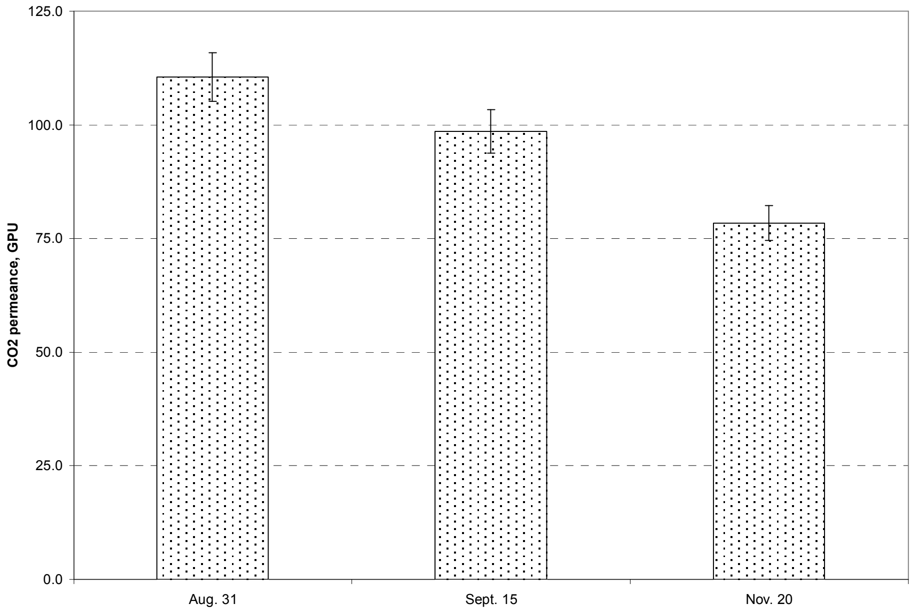

Fig. 3: Change in CO_2 permeance with time. Module, Cardo-type polyimide module; feed pressure, 100 psig

3.1.2. Separation experiments with CO_2/CH_4 gas mixtures

Separation experiments were carried out in the following order of CO_2 mole fraction in the feed gas: pure CH_4, 5% CO_2, 10% CO_2, 24.6% CO_2 (the balance being CH_4) and pure CO_2. The obtained results are summarized in Figures 4 and 5.

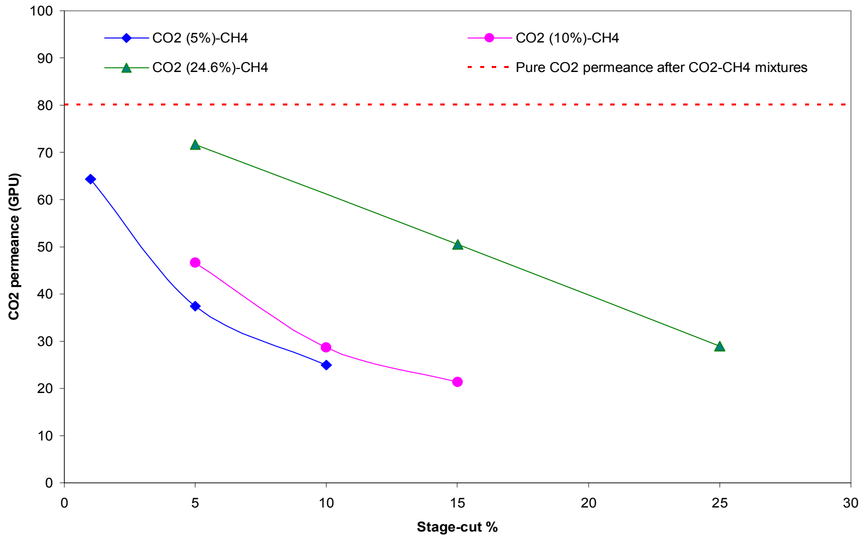

Fig. 4: CO_2 permeance versus stage-cut for various feed CO_2 concentrations. Module, Cardo-type polyimide module; feed pressure, 100 psig.

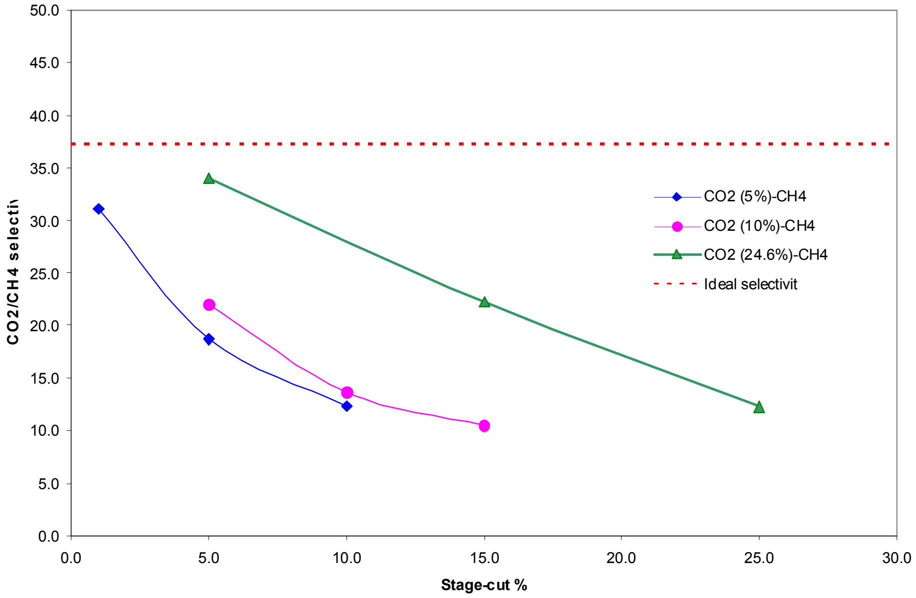

Fig. 5: CO_2/CH_4 permselectivity versus stage-cut for various feed CO_2 concentrations. Module, Cardo-type polyimide module; feed pressure, 100 psig

It is shown in Figure 4 that CO_2 permeance decreases with an increase in stage-cut for all CO_2 concentrations and this is the stage-cut effect. This effect could be due to the changing in the retentate concentration along the fibers. It should be noted that polarization effect increases at higher stage-cuts too.

The CO_2 permeances at lower stage–cuts are close to the pure CO_2 permeance (that was done after CO_2/CH_4 experiments) even for a CO_2 feed concentration of 5 %. Figure 5 shows also that CO_2/CH_4 permselectivity is very close to the ideal CO_2/CH_4 permselectivity, which is calculated based on the pure CH_4 experiment result at 100 psig before CO_2/CH_4 experiments and pure CO_2 after CO_2/CH_4 experiments, at low stag-cuts, especially a CO_2 concentration of 24.6 %.

Looking into Figures 4 and 5 closely, it is found, interestingly, that, similar values for both CO_2 permeance and CO_2/CH_4 separation factor were obtained when the stage-cuts were equal to the feed CO_2 volume per cent, regardless of the feed CO_2 concentration.

3.2. Polyphenylene oxide (PPO) hollow fibers

3.2.1. Pure gas permeation experiments

The obtained results of pure gas permeation tests through commercial PPO hollow fibers at ambient temperature are summarized in Table 3. These results were obtained by one PPO module (PPO#1) that was chosen to be used in the gas mixture experiments as well.

As it is shown in Table 3, pure CO_2 and O_2 permeances and CO_2/CH_4 permeation ratio increased with an increase in the feed pressure, whereas O_2/N_2 permselectivity did not change. As well, both N_2 permeance after O_2 experiments and CH_4 permeance after CO2 experiments are higher than those before O_2 and CO_2 exposure. These results can be expected. For these PPO hollow fibers the CO_2 and CH_4 permeances did not change during three months of experiments.

Table 3. Permeances and Permselectivities of PPO hollow fibers for gas pairs O2/N2 and CO2/CH4

	Permeance (GPU)						Permselectivity	
Feed Pressure (Psig)	N2	O2	N2 (after O2)	CH4	CO2	CH4 (after CO2)	CO2/CH4	O2/N2
50	9.5	37	9.5 (9.6)	11.1	180		16.2	3.9
75	10.0	39	10.3 (10.4)	11.9	194		16.3	3.9
100	10.7	42	10.5 (10.5)	12.7	211	12.9 (13.0)	16.7	3.9

The data in parenthesis are obtained immediately after the start of the experiments.

3.2.2. Separation experiments with CO_2/CH_4 gas mixtures

Separation experiments were carried out in the following order of CO_2 mole fraction in the feed gas: pure CH_4, 5% CO_2, 10% CO_2, 24.6% CO_2 (the balance being CH_4) and pure CO_2. The obtained results are shown in Figures 6 and 7. It can be seen that, the CO_2 permeance increases with feed CO_2 volume % (i.e. CO_2 partial pressure in feed).

Looking into Figures 6 and 7 closely, it can be concluded again that similar CO_2 permeance and separation factor were obtained when the stage-cut was equal to the feed gas volume %, regardless of the feed CO_2 concentration.

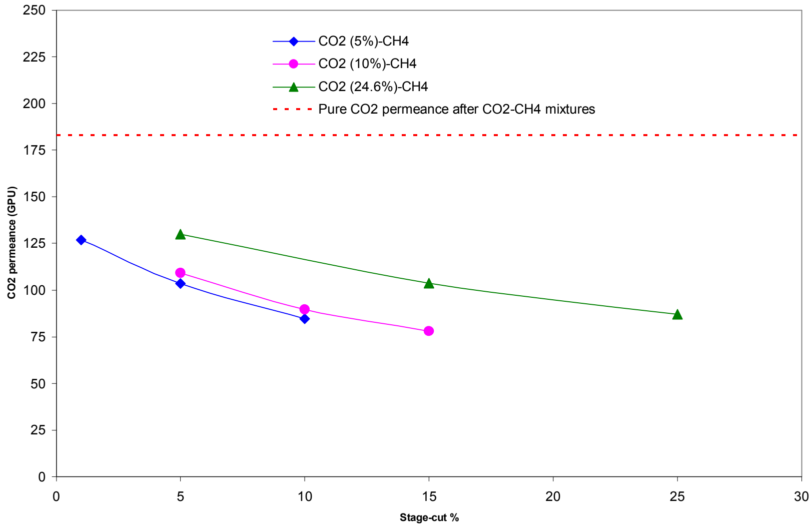

Fig. 6: CO_2 permeance versus stage-cut for various feed CO_2 concentrations. Module, PPO module; feed pressure, 100 psig

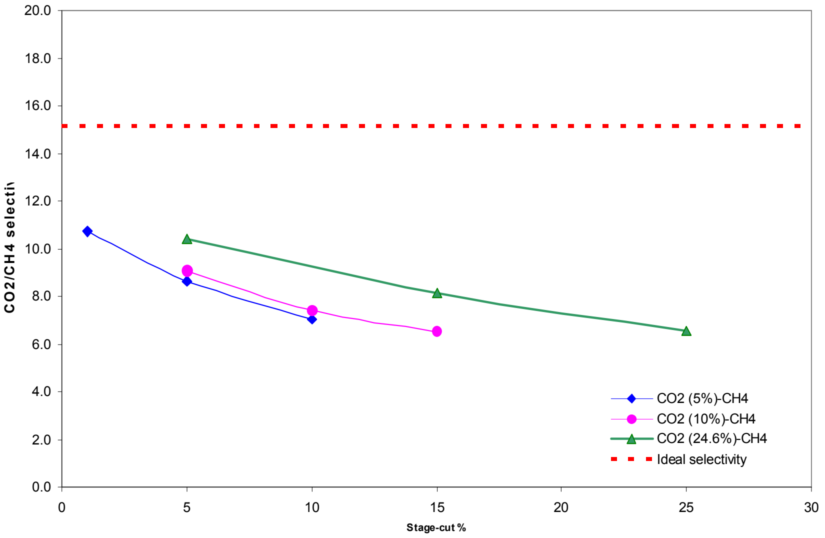

Fig. 7: CO_2/CH_4 permselectivity versus stage-cut for various feed CO_2 concentrations. Module, PPO module; feed pressure, 100 psig

For PPO hollow fibers, the CO_2 permeance and CO_2/CH_4 permselectivity are not very close to those obtained for pure gases. This is consistent with CO_2 plasticization effect in pure gas case (Table 3).

3.3. Selectivity and permeance plot

Figure 8 shows ideal selectivity versus permeance plots for these two types of membrane modules (RITE-A and PPO#1). It can be seen that these two membranes have special advantages fro gas separations based on high gas permeation rate and moderate selectivity of PPO and high selectivity and moderate gas permeation rate of Cardo-type polyimide modules.

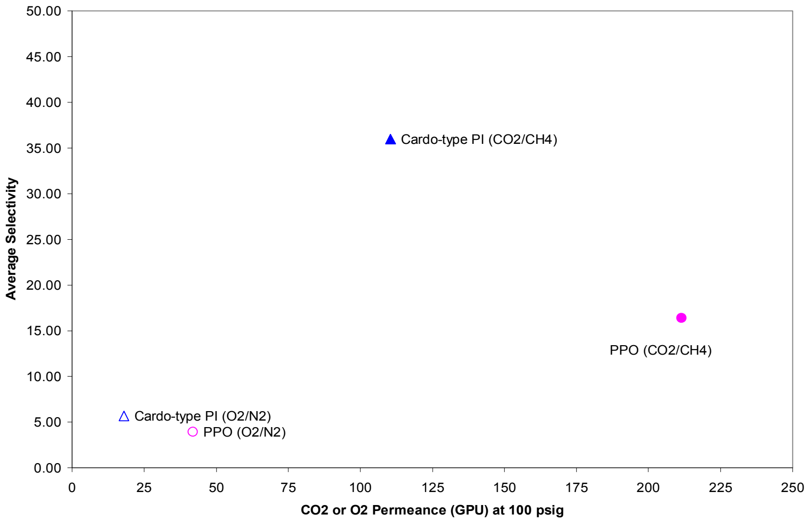

Fig. 8: Selectivity versus permeance for Cardo-type polyimide hollow fiber module and PPO hollow fiber module. Feed pressure, 100 psig

4. Conclusions

From the above mentioned experiments, it can be concluded that Cardo-type polyimide hollow fiber membranes have high CO_2/CH_4 and O_2/N_2 selectivity, and high or moderate CO_2 and O_2 permeability. On the other hand, PPO hollow fibers have low-to- moderate selectivity, but very high CO_2 permeability.

Although Cardo-type polyimides were developed for CO_2/N_2 and PPO hollow fibers were commercialized for O_2/N_2 separations, Cardo-type polyimidies can also be good candidates for O_2/N_2 separation.

Another conclusion from this investigation is that experimental data for the permeance as well as the separation factor can not compared easily when they are taken at a given stage-cut. On the other hand, the data are almost the same when the stage-cut is set equal to the feed gas volume percent. Hence it is proposed to maintain the stage-cut equal to the feed gas volume per cent in order to collect data that are mutually comparable.

References:

[1] J. K. Mitchell, “On the permeation of gases”, Am. J. Med. Sci., 25 (1833), 100-112.

[2] T. Graham, “On the absorption and dialytic separation of gases by colloid”, Septa. Phil. Mag., 32 (1866), 401-420.

[3] S. Loeb and S. Sourirjan, “Sea water demineralization by means of an osmotic membrane”, Advan. Chem. Ser., 38 (1962), 117-132

[4] J. P. Agrawal and S. Sourirajan, “Helium separation by cellulose acetate membranes”, J. Appl. Polym. Sci., 13 (1969), 1065-1068.

[5] J. P. Agrawal and S. Sourirajan, “High-flux freeze-dried cellulose acetate reverse osmosis membranes as micro-porous barriers in gas permeation and separation”, J. Appl. Polym. Sci, 14 (1970), 1303-1321.

[6] L. M. Robeson, “Correlation of separation factor versus permeability for polymeric membranes”, J. Memb. Sci., 62 (1991), 165-185.

[7] L. M. Robeson, “Polymer membranes for gas separation”, Current Opinion in Solid State and Materials Sci., 4 (1999), 549-552.

[8] J. Smid, J. H. M. Albers, P. M. Kusters, “The formation of asymmetric hollow fibre membranes for gas separation, using PPE of different intrinsic viscosities”, J. Memb. Sci., 64 (1991), 121-128.

[9] J. D. Wind, D. R. Paul, W. J. Koros, “Natural gas permeation in polyimide membranes”, J. Memb. Sci., 228 (2004), 227-236.

[10] J. H. M. Albers, J. Smid, A. P. M. Kusters, “Gas separation apparatus and also method for separating gases means of such an apparatus”, U. S. Patent 5,129,920 (1992).

[11] S. Karashima, Y. Tokuda, A. Tachiki, K. Takagi, K. Haraya and C. Kamizawa, “Development of Cardo-type polyimide hollow fiber membranes for CO2 separation”, Greenhouse gas control technologies, P. Riemer, B. Eliasson and A. Wokaun, editors, Elsevier Sci. Ltd., 1999, 1032-1037.

[12] S. Kazama, T. Teramoto, K. Haraya, “Carbon dioxide and nitrogen transport properties of bis(phenyl)fluorine-based Cardo polymer membranes”, J. Memb. Sci., 207 (2002), 91-104.

[13] Y. Tokuda, E. Fujisawa, N. Okabyashi, N. Matsumiya, K. Takagi, H. Mano, K. Haraya and M. Sato, “Development of hollow fiber membranes for CO_2 separation”, Energy Convers. Mgmt., 38(1997), S111-S116.
[14] Y. Hirayama, S. Kazama, E. Fujisawa, M. Nakabayashi, N. Matsumiya, K. Takagi, K. Okabe, H. Mano, K. Haraya and C. Kamizawa, “Novel membranes for carbon dioxide separation”, Energy Convers. Mgmt., 36(1995), 435-438.
[15] N. A. Plate and Y. Yampolskii, “High free volume polymers”, in Polymer Gas Separation Membranes, Eds. D. R. Paul and Y. Yampolskii, CRC Press, London, 1994, p. 156.
[16] D. Aycock, “Polyphenylene ether”, in Encyclopedia of Polymer Science and Technology, Vol. 13, Wiley Interscience Publishers, New York, NY, 1974.
[17] G. Chowdhury, R. Vujosevic, T. Matsuura, B. Laverty, “Effects of polymer molecular weight and chemical modification on the gas transport properties of poly (2, 6-dimethy –1 , 4- phenylene oxide)”, J. Appl. Polym. Sci., 77 (2000), 1137-1143.
[18] W. A. Dietz, “Response factors for gas chromatographic analyses”, J. of G.C., Feb. 1967, 68-71