

# CO<sub>2</sub> Permeability through Carbon Hollow Fiber Membranes from Atmospheric Pressure up to 56 bar

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**Abstract**—Two asymmetric carbon hollow fiber membranes were prepared and tested from low, atmospheric, to high pressures, up to ~56 bars, CO<sub>2</sub> permeance measurements. Both membranes were produced via pyrolysis, at inert environment, at 1050 °C, while the one was activated with CO<sub>2</sub> at the higher pyrolysis temperature. The carbon dioxide was chosen for the permeance performance of the studied membranes. A maximum in the permeance versus equilibrium pressure curve is observed in the case of CO<sub>2</sub>. This phenomenon has close analogy to the case of mesoporous membranes. The result shows that the CO<sub>2</sub> provides a maximum in the permeance values. This weakens considerably as the membrane ultra-microporosity is increased. The high pressure permeability study may be potentially useful for the identification of the optimal pressure and temperature conditions for efficient gas separations.

**Keywords**—Carbon dioxide; CO<sub>2</sub> capture; High permeance; High pressure; Optimum operating pressure.

## I. INTRODUCTION

THE groups, which work on the area of the membrane technology worldwide, are many. Among the other fields of the membrane research areas the gas separation processes and singularly the CO<sub>2</sub> separation are in the first priority of the industry and the governments. The air separation, the olefin/paraffin separation, the landfill gas recovery, the natural gas processing, the helium and hydrogen recovery, the carbon dioxide/nitrogen etc are some of the many areas where membranes are candidates for use [1].

The most popular materials for the membrane technology are: metal membranes [2], polymeric membranes [3], ceramic and zeolites membranes [4,5] and also mixed-matrix membranes [6–9]. In addition polymeric membrane materials

have seemingly reached a limit in the productivity-selectivity tradeoff despite the concentrated efforts to tailor polymer structures to change separation properties [10,11].

One of the main targets for the membrane development is the production of robust membranes with higher both selectivities and permeabilities [12]. To this end the evaluation of the permeation behavior of the membranes at a wide range of pressures is imperative. However, the works, which are referred in the literature relevant to the effect of the working pressure on the permeation and separation properties of both inorganic and polymeric membranes, are limited. In the case of polymeric membranes the plasticization phenomenon during the CO<sub>2</sub> presence has been studied mainly for glassy polymers [13] such as polyimide and blends membranes. For example, Kapantaidakis et al. reported that in ultra-thin asymmetric PI and PS/PI blends hollow fibers show accelerated pure CO<sub>2</sub> plasticization phenomena and subsequent reduction of the ideal CO<sub>2</sub>/N<sub>2</sub> permselectivity. On the other hand, in the case of CO<sub>2</sub>/N<sub>2</sub> binary mixture permeation, the plasticization behavior is suppressed due to competitive sorption of N<sub>2</sub> [14]. Permeability measurements through mesoporous media have been published exhibiting a maximum at some relative pressure, a fact that has been attributed to the occurrence of capillary condensation in the main body of the mesopores [15–17]. Maximum at permeability values were also observed by Katsaros et al. where two microporous carbon membranes were studied, with a pore size of about 8 Å each, in the case of CO<sub>2</sub> at 310 K. The maxima on CO<sub>2</sub> permeability were observed at 37 and 28 bar for Membrane 1 and Membrane 2 respectively [18].

In the current study two carbon membranes, carbon hollow fiber membranes were tested with CO<sub>2</sub> permeance experiments at 307 K. The experiments took place at pressures from 1 bar up to ~56 bars. At both cases the differential permeance experiments show that the increase of the equilibrium pressure has positive action on the permeance coefficients until a critical pressure where the increase of the equilibrium pressure has negative action on the carbon dioxide permeance coefficients. This behavior results to the optimum operating pressure where these membranes can be used for the maximum CO<sub>2</sub> separation factors.

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## II. EXPERIMENTAL

### A. Membrane Preparation

The studied membranes were prepared by carbonization at controlled environment of asymmetric polyimide hollow fiber precursors membranes. The maximum pyrolysis temperature was 1323 K at both cases. In the case of M3 membrane an extra stream of pure CO<sub>2</sub> was applied at the higher temperature for 1 min. More details relevant to the materials preparation and their physicochemical characterization were described previously [19].

### B. Permeance Experiments

All the permeance measurements occurred in a metal closed type apparatus described previously [20,21]. The up limit of the apparatus is 60 bars while the instrumentation is equipped with high sensitive pressure transmitters making capable the experiments at the high vacuum.

## III. RESULTS AND DISCUSSION

In the current work we choose the CO<sub>2</sub> as the studied gas because of the very important role which has as an environmental pollutant as well as because it is a molecule with high interest as industrial gas for many applications, especially at pressures more than the atmospheric conditions [22,23]. The carbon dioxide is a gas with linear configuration with highly scientific and industrial interest thanks to their unusual physical properties (see Fig. 1). In specific the density of the CO<sub>2</sub> can vary importantly even with slight change of the pressure and temperature. In Figure 1 approximate molecular dimensions of CO<sub>2</sub> are shown. These dimensions were estimated using published force fields for molecule-molecule interactions [24,25].

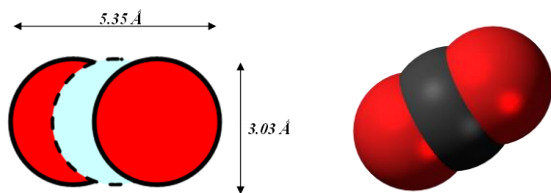


Fig. 1. Illustrations showing the 3D structure and the approximate dimensions of CO<sub>2</sub> molecule (3D structure is from Wikipedia pages).

Using the CO<sub>2</sub> as the gas for our permeance experiments we choose to work at a temperature slightly higher than the critical temperature of the CO<sub>2</sub>. A good tool for the approximation and the evaluation of the optimum “working” pressure of a membrane is the differential permeability experiment. By this way we can predict the pressure where the membrane giving the best selectivity coefficients, in a wide range of pressure, from mbars up to the instrument limits (in our case up to 60 bars). In this kind of experiments first the membranes evacuated and the first gas permeance measurement took place at low feed pressure, 1 bar. Following the membranes are equilibrated at the same pressure (0–55.64 bar) on both sides.

At a next step the membranes are isolated from the gases tanks by closing all the references valves and the high pressure section is pressurized to approximately 1 bar higher than the low pressure section. Subsequently, the valves adjacent to each membrane are opened and gas is allowed to permeate through the porous structure while the pressure increasing is monitored by the differential pressure manometer [18]. The CO<sub>2</sub> permeances at each equilibrium pressure are presented in Table 1.

TABLE I  
CO<sub>2</sub> PERMEANCES THROUGH THE CFM<sub>5</sub> AT VARIOUS PRESSURES

Pressure	PERMEANCE (GPU)		
	M1	M3	INCREASE FACTOR M1 / M3
1	31.8	120.6	1 / 1
2	58.2	244.1	1.8 / 2.0
4	105.9	396.3	3.3 / 3.3
6.05	175.9	506.8	5.5 / 4.2
8.6	225.8	589.3	7.1 / 4.9
10.55	243.2	637.6	7.7 / 5.3
12.95	272.8	679.2	8.6 / 5.6
15.55	319.0	695.0	10.0 / 5.8
16.37	306.9	731.7	9.7 / 6.0
17.45	314.9	724.2	9.9 / 6.0
20.2	333.7	748.5	10.5 / 6.2
23	352.5	751.2	11.1 / 6.2
25.75	373.8	761.8	11.8 / 6.3
28.85	398.4	758.6	12.5 / 6.3
33	412.9	765.1	13.0 / 6.3
37.6	402.6	735.0	12.7 / 6.0
42.13	410.1	709.7	12.9 / 5.9
46.8	406.1	672.8	12.8 / 5.6
55.64	400.1	573.1	12.6 / 4.8

As we can see in Table 1 the permeance coefficients starts from the 31.8 and increase up to 412.9 GPU in the case of M1 membrane while the M3 membrane, which presents higher permeance coefficients, performs CO<sub>2</sub> permeance of 120 GPU at equilibrium pressure of 1 bar and the higher permeance of 765 GPU occurred at 33 bars.

The studied membranes are two carbon hollow fiber membranes with extended microporous structure. On the other hand, as we have investigated in our previous work [19], both membranes present porosity in the mesoporous region. In addition, the separating layer of the M3 membrane contains mesopores with size above 34 nm, whereas for the M1 membrane the coexisting mesopores are smaller than 3.5 nm. This difference in the pore size of the membranes is reflected on the Figure 2, where is clear that the membrane with the bigger pores (M3) occurs a maximum at the permeance at 32 bar and the increase of the pressure resulting in decrease of the permeances. This is because of the decrease of the diffusion of the CO<sub>2</sub> due to the role of scattering from fluid–fluid collisions, which dominate over the solid-fluid collisions because of the smoothness of the carbon-fluid potential-energy surface [26]. This is in good agreement with the result that the self-diffusion coefficient decreases with

concentration, whilst the Darken transport diffusion coefficient passes through a maximum [27]. The concentration increases as the pore diameter increases and therefore the CO<sub>2</sub> molecules become fewer motives and therefore the further increase of the pressure results in lower permeance coefficients.

In Figure 2 the increase factor–pressure plot describes the effect of the equilibrium pressure on the CO<sub>2</sub> permeation properties at 307 K, temperature higher than the critical temperature of the CO<sub>2</sub>,  $T_{C(CO_2)} = 304.107$  K [28] and at a wide range of pressures, from 1 up to ~55 bar ( $1 \leq P \leq 56$  bar).

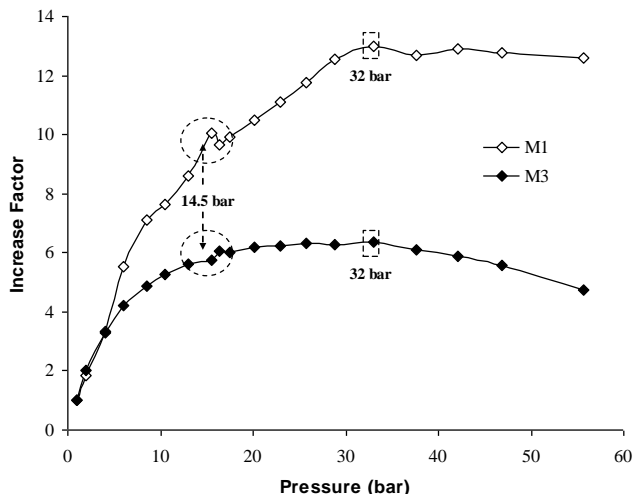


Fig. 2. The effect of feed pressure on CO<sub>2</sub> permeation properties for M1 and M3 carbon hollow fiber membranes. (The "Increase Factor" is the ratio of the CO<sub>2</sub> permeance at each feed pressure concerning to the permeance at feed pressure of 1 bar.)

As we can see both membranes present a maximum permeance increasing at the pressure of 32 bars while at the pressure of 14.5 bar a small-instant peak was observed at both cases. This small "unstable" increase of the permeance at this low equilibrium pressure probably becomes due to the rearrangement of the linear gas molecule according to the better molecule packing into the pores. In the case of M1 membrane the increase factor is about twofold that in the case of M3 membrane as well as a plateau on the permeance values was observed at pressures higher than 35 bars.

#### IV. CONCLUSION

The present study, we have performed CO<sub>2</sub> permeance measurements at 307 K for two microporous carbon hollow fiber membranes and at pressures up to ~56 bars. The differential permeance measurements show that there is a pressure at each membrane where the CO<sub>2</sub> permeance coefficient presents maximum values. This phenomenon could be explained by taking into consideration the strong differences in the CO<sub>2</sub> densities during the increase of the pressure. At 307 K, temperature above the critical temperature of the studied gas ( $T_c = 304.107$  K), the CO<sub>2</sub> is able to form a liquid like phase. According to the shape, the size and the pore

network the pressure, where the carbon dioxide molecules have the maximum mobility, has changed. In our cases the pressure with the maximum permeance coefficients is 32 bars for both M1 and M3 carbon hollow fiber membranes. This result can be of significant importance for determining the optimum operating conditions and indicates possible uses of the microporous carbon membranes in specific CO<sub>2</sub> separation applications by supercritical liquefaction.

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#### REFERENCES

- [1] P. Bernardo, E. Drioli, G. Golemme, "Membrane Gas Separation: A Review/State of the Art," *Ind. Eng. Chem. Res.* vol. 48, no. 10, pp. 4638–4663, April 2009. <http://dx.doi.org/10.1021/ie8019032>
- [2] G. Alefeld and J. Völkl (editors), "Hydrogen in Metals I: Basic Properties," Springer-Verlag, Germany 1978. <http://dx.doi.org/10.1007/3-540-08705-2>
- [3] U. Merten and P.K. Gantzel, "Method and Apparatus for Gas Separation by Diffusion," US Patent 3,415,038 (1968).
- [4] J. Caro, M. Noack, P. Kolsch, R. Schäfer, "Zeolite membranes – state of their development and perspective," *Micropor. Mesopor. Mater.* vol. 38, no. 1, pp. 3–24, July 2000. [http://dx.doi.org/10.1016/S1387-1811\(99\)00295-4](http://dx.doi.org/10.1016/S1387-1811(99)00295-4)
- [5] J. Brinker, C.-Y. Tsai and Y. Lu, "Inorganic Dual-Layer Microporous Supported Membranes," US Patent 6,536,604 (2003).
- [6] H.J.C. te Hennepe, D. Bargeman, M.H.V. Mulder, C.A. Smolders, "Zeolite-filled silicone rubber membranes: Part 1. Membrane preparation and pervaporation results," *J. Membr. Sci.* vol. 35, pp. 39–55, December 1987. [http://dx.doi.org/10.1016/S0376-7388\(00\)80921-7](http://dx.doi.org/10.1016/S0376-7388(00)80921-7)
- [7] E. K. Chatzidaki, E. P. Favvas, S. K. Papageorgiou, N. K. Kanellopoulos, N. V. Theophilou, "New polyimide–polyaniline hollow fibers: Synthesis, characterization and behavior in gas separation," *Europ. Pol. J.* vol. 43, pp. 2010–2016, December 2007. <http://dx.doi.org/10.1016/j.eurpolymj.2007.09.005>
- [8] Chengwen Song, Tonghua Wang, Xiuyue Wang, Jieshan Qiu, Yiming Cao, "Preparation and gas separation properties of poly(furfuryl alcohol)-based C/CMS composite membranes," *Separ. Purif. Technol.* vol. 58, pp. 412–418, January 2008. <http://dx.doi.org/10.1016/j.seppur.2007.05.019>
- [9] E. P. Favvas, S. F. Nitodas, A. Stefanopoulos, K. L. Stefanopoulos, S. K. Papageorgiou, A. Ch. Mitropoulos, "High Purity Multi-Walled Carbon Nanotubes: Preparation, Characterization and Performance as Filler Materials in co-polyimide Hollow Fiber Membranes," *Separ. Purif. Technol.* vol. 122, pp. 262–269, February 2014. <http://dx.doi.org/10.1016/j.seppur.2013.11.015>
- [10] De Q. Vu, W. J. Koros, S. J. Miller, "High Pressure CO<sub>2</sub>/CH<sub>4</sub> Separation Using Carbon Molecular Sieve Hollow Fiber Membranes," *Ind. Eng. Chem. Res.* vol. 41, pp. 367–380, 2002. <http://dx.doi.org/10.1021/ie010119w>
- [11] C. M. Zimmerman, A. Singh, W. J. Koros, "Tailoring mixed matrix composite membranes for gas separations," *J. Membr. Sci.* vol. 137, pp. 145–154, December 1997. [http://dx.doi.org/10.1016/S0376-7388\(97\)00194-4](http://dx.doi.org/10.1016/S0376-7388(97)00194-4)
- [12] M.B. Kao, S. Sircar, "Nanoporous carbon membranes for separation of gas mixtures by selective surface flow," *J. Membr. Sci.* vol. 85, pp. 253–264, December 1993. [http://dx.doi.org/10.1016/0376-7388\(93\)85279-6](http://dx.doi.org/10.1016/0376-7388(93)85279-6)

- [13] J. S. Chiou, J. W. Barlow, D. R. Paul, "Plasticization of glassy polymers by CO<sub>2</sub>," *J. Appl. Polym. Sci.* vol. 30, pp. 2633–2642, June 1985.  
<http://dx.doi.org/10.1002/app.1985.070300626>
- [14] G. C. Kapantaidakis, G. H. Koops, M. Wessling, S. P. Kaldis, G. P. Sakellariopoulos, "CO<sub>2</sub> Plasticization of Polyethersulfone/ Polyimide Gas-Separation Membranes," *AIChE* vol. 49, pp. 1702–1711, July 2003.  
<http://dx.doi.org/10.1002/aic.690490710>
- [15] H. Rhim, S.-T. Hwang, "Transport of capillary condensate," *J. Colloid Interface Sci.*, vol. 52, pp. 174–184, July 1975) 174.
- [16] K.-H. Lee, S.-T. Hwang, "The transport of condensible vapors through a microporous vycor glass membrane," *J. Colloid Interface Sci.* vol. 110, pp. 544–555, April 1986.  
[http://dx.doi.org/10.1016/0021-9797\(86\)90407-8](http://dx.doi.org/10.1016/0021-9797(86)90407-8)
- [17] R.J.R. Uhlhorn, K. Keizer, A.J. Burggraaf, "Gas transport and separation with ceramic membranes. Part I. Multilayer diffusion and capillary condensation," *J. Membr. Sci.* vol. 66, pp. 259–269, February 1992.  
[http://dx.doi.org/10.1016/0376-7388\(92\)87016-Q](http://dx.doi.org/10.1016/0376-7388(92)87016-Q)
- [18] F. K. Katsaros, T. A. Steriotis, A. K. Stubos, A. Mitropoulos, N. K. Kanellopoulos, S. Tennison, "High pressure gas permeability of microporous carbon membranes," *Microporous Materials* vol. 8, pp. 171–176, February 1997.  
[http://dx.doi.org/10.1016/S0927-6513\(96\)00080-6](http://dx.doi.org/10.1016/S0927-6513(96)00080-6)
- [19] E. P. Favvas, G. E. Romanos, S. K. Papageorgiou, F. K. Katsaros, A. Ch. Mitropoulos, N. K. Kanellopoulos, "A Methodology for the morphological and physicochemical characterization of asymmetric carbon hollow fiber membranes," *J. Membr. Sci.* vol. 375, pp. 113–123, June 2011.  
<http://dx.doi.org/10.1016/j.memsci.2011.03.028>
- [20] E. K. Chatzidaki, E. P. Favvas, S. K. Papageorgiou, N. K. Kanellopoulos and N. V. Theophilou "New Polyimide – Polyaniline Hollow Fibers: Synthesis, Characterization and behavior in Gas Separation," *Eur. Polym. J.* vol. 43, pp. 5010–5016, December 2007.  
<http://dx.doi.org/10.1016/j.eurpolymj.2007.09.005>
- [21] S. F. Nitodas, E. P. Favvas, G. E. Romanos, M. A. Papadopoulou, A. Ch. Mitropoulos and N. K. Kanellopoulos "Synthesis and Characterization of Hydrogen Selective Silica-based Membranes," *J. Porous Mater.* vol. 15, pp. 551–557, October 2008.  
<http://dx.doi.org/10.1007/s10934-007-9132-4>
- [22] G. T. Farmer, John Cook, *Introduction to Earth's Atmosphere in "Climate Change Science: A Modern Synthesis,"* New York: Springer, 2013, pp. 199–213, ch. 8.  
<http://dx.doi.org/10.1007/978-94-007-5757-8>
- [23] D. Berstad, R. Anantharaman, P. Nekså, "Low-temperature CO<sub>2</sub> capture technologies – Applications and potential," *Intern. J. Refriger.* vol. 36, pp. 1403 – 1416, August 2013.  
<http://dx.doi.org/10.1016/j.ijrefrig.2013.03.017>
- [24] R. Krishna, J. M. van Baten, E. García-Pérez, S. Calero, "Diffusion of CH<sub>4</sub> and CO<sub>2</sub> in MFI, CHA and DDR zeolites," *Chem. Phys. Lett.* vol. 429, pp. 219–224, September 2006.  
<http://dx.doi.org/10.1016/j.cplett.2006.08.015>
- [25] S. Li, J. L. Falconer, R. D. Noble, R. Krishna, "Modeling Permeation of CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, and N<sub>2</sub>/CH<sub>4</sub> Mixtures Across SAPO-34 Membrane with the Maxwell-Stefan Equations," *Ind. Eng. Chem. Res.* vol 46, pp. 3904–3911, June 2007.  
<http://dx.doi.org/10.1021/ie0610703>
- [26] A. I. Skoulidas, D. S. Sholl, J. K. Johnson, "Adsorption and diffusion of carbon dioxide and nitrogen through single-walled carbon nanotube membranes," *J. Chem. Phys.* vol. 124, 054708, February 2006.  
<http://dx.doi.org/10.1063/1.2151173>
- [27] D. Nicholson, R. Cracknell, N. Quirke, "A Transition in the Diffusivity of Adsorbed Fluids through Micropores," *Langmuir* vol. 12, pp. 4050–4052, August 1996.  
<http://dx.doi.org/10.1021/la960179k>
- [28] V. Vesovic, W. A. Wakeham, G. A. Olchowy, J. V. Sengers, J. T. R. Watson, J. Millat, "The Transport Properties of Carbon Dioxide," *J. Phys. Chem. Ref. Data* vol. 19, pp. 763–808, May 1990.  
<http://dx.doi.org/10.1063/1.555875>