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Research Article

Separation of CO₂/N₂ by Means of a Carbon Membrane

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The permeation and separation performance of an ultramicroporous carbon membrane for separation of CO₂/N₂ mixtures were investigated. The experiments were conducted using the steady-state measurement method with pure gases (dead-end mode) and a CO₂/N₂ gas mixture (20/80 mol.-%) (cross-flow mode) in the temperature range from 293 K to 363 K and at feed pressures of up to 1.4 MPa and atmospheric pressure on the permeate side. The membrane exhibited a selectivity of about 25 and permeability of about 500 Barrer for CO₂ in the mixture with N₂. The single-gas measurements do not reflect the membrane performance correctly. An adsorption-selective effect is assumed to be the main separation mechanism. Moreover, membrane-aging effects causing blocking due to pore constrictions through adsorption were observed. These pore constrictions lower the permeability, but they raise the selectivity. Operation at high temperatures leads to a reduction of aging effects.

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1 Introduction

Membrane separation of gas mixtures meets with rising interest because of its great significance for industrial applications. Membrane processes are frequently an energy- and space-saving alternative to conventional separation technologies. Furthermore, an easy scale-up makes membrane processes attractive for plant designers and manufacturers. For CO₂ separation from flue gases a CO₂/N₂ selectivity of 70 and a CO₂ permeance of at least $3.3 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ are required to achieve an economical operation [1]. Polymeric membranes in most cases reach the required performance at temperatures below 313 K, but they indicate a dramatic loss in selectivity at higher requisite operating temperatures as well as sensitivity to acid gases such as SO₂. Therefore, installations of scrubbers and devices to lower the flue gas temperature are necessary for successful application of these materials.

Inorganic membranes, especially carbon membranes, have proved to be promising candidates for CO₂ separation from flue gas streams. In comparison to other gas separation membranes like polymeric materials, carbon membranes provide better selectivity, heat resistance, and chemical stability. Numerous types of carbon membranes manufactured by chemical vapor deposition [2, 3], chemical vapor infiltration

[4, 5], or pyrolysis of polymeric precursors [6–10] are presented in literature. Different kinds of post-treatment lead to different permeation behaviors and transform a molecular sieving membrane into an adsorption-selective carbon membrane with tailored properties. One of the advantages of carbon membranes compared with other ultramicroporous inorganic membranes for gas separation like zeolite is that they are relatively easy to prepare and also to repair if damaged. This makes them potentially attractive for a number of industrial applications as well as for CO₂ separation from flue gases.

Due to the large variety of membrane-manufacturing possibilities (used precursors, carbonization, and post-treatment conditions) as well as the chosen gas-testing conditions, the comparison of the carbon membranes already presented in literature is rather difficult. Furthermore, the difference between single-gas and gas-mixture experiments as well as the aging grade of the tested membrane have to be considered, but unfortunately are not reported by many authors. Despite of the above-mentioned facts, the tendency of carbon membranes for CO₂/N₂ separation is determinable. The smaller and more adsorbable CO₂ molecule permeates preferentially through the membrane so that selectivities between 8 and 95 can be achieved at still reasonable permeability values of up to 800 Barrer ($1 \text{ Barrer} = 3.348 \cdot 10^{-19} \text{ kmol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) [11–13]. Moreover, the impact of impurities commonly found in industrial streams like water, H₂S, CO, and hexane was investigated by many authors [14, 15]. On the whole, relatively limited reductions in the membrane performance were observed, a fact promising wide application possibilities.

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The first step of this study was to evaluate the use of carbon membranes (provided by the Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Hermsdorf branch of the institute) for CO₂/N₂ separation in laboratory scale. Single gas permeances as well as the mixed gas separation performance of the carbon membrane, using pressurized feed (up to 1.4 MPa) and atmospheric permeate, were obtained in a temperature range from 293 K to 363 K.

2 Experimental Methods

Amorphous carbon or graphite-like carbon is plane-structured with a defined lattice plane distance of 0.34 nm. Because of their brittleness, the carbon membranes were synthesized on porous alumina tubes by dipcoating the tubes in a polymeric precursor solution and pyrolysis at temperatures above 873 K in an inert atmosphere [16]. The tubes had an inner diameter of 7 mm, an outer diameter of 10 mm, and a length of 250 mm. The membrane tube was mounted in a stainless-steel module and sealed at both ends with O-rings (NBR 90).

A schematic illustration of the setup is presented in Fig. 1. The permeation and separation properties of the membranes were examined using the steady-state measurement method with pure gases (dead-end mode) and a CO₂/N₂ gas mixture (20/80 mol.-%; cross-flow mode) in a temperature range from 293 K to 363 K and at feed pressures of up to 1.4 MPa and atmospheric pressure on the permeate side. Permeate and retentate flows were detected by means of Coriolis-type mass flow meters. The pressure on each side of the membrane was independently detected and controlled. The membrane module temperature was controlled with a heating jacket.

Pure CO₂ and N₂ (purity grade 5.0) were purchased from Praxair GmbH (Hürth, Germany). The feed gas mixtures with defined composition were supplied from the gas bottle (Praxair, Hürth, Germany). The composition of permeate and retentate streams was analyzed by online gas chromatography equipped with a mass spectrometry detector (GCMS-QP 2010 Plus, Shimadzu).

The dependencies of membrane permeation and separation performance on the operating pressure and temperature were investigated. Considering the feed and permeate composition,

the permeance can be calculated according to the following equation:

$$Q_i = \frac{J_i}{\Delta P_i} \quad (1)$$

where J_i (mol s⁻¹ m⁻²) and ΔP_i (Pa) are the permeate flux and the partial pressure difference of the components between the feed and permeate bulk mixtures, respectively. For single gas experiments the transmembrane pressure difference was used for permeance calculations.

The ideal selectivity is the ratio of the single-gas permeances. The CO₂/N₂ separation factor for mixtures after reaching steady-state conditions was calculated as follows:

$$\alpha_{\text{CO}_2/\text{N}_2} = \frac{y_{\text{CO}_2}/y_{\text{N}_2}}{x_{\text{CO}_2}/x_{\text{N}_2}} \quad (2)$$

where y means the mole fractions of the components in the permeate stream and x in the feed stream.

3 Results and Discussion

3.1 Effect of the Operating Pressure

Fig. 2 illustrates the CO₂ and N₂ single gas permeances as well as the mixture gas permeances as a function of the feed pressure at 293 K. The tested carbon membrane exhibited a good permeance and high selectivity for CO₂.

The permeance of CO₂ proved to be higher than that of nitrogen in all experiments with pure gases and gas mixtures. However, the transport of components through the membrane in a gas mixture is totally different from that obtained with pure gases. On the one hand, the permeance of both components in the mixture decreases slightly with increasing feed pressure, contrary to the permeation behavior of pure gases. On the other hand, the CO₂ permeance indicates higher values for mixtures compared to the pure gas, whereas the N₂ permeance decreases. Therefore, the selectivity of the binary mixture is significantly higher than the ideal selectivity. The maximum of the CO₂/N₂ gas mixture selectivity was measured at 1.4 MPa and 293 K and reached a value of 25, whereas the

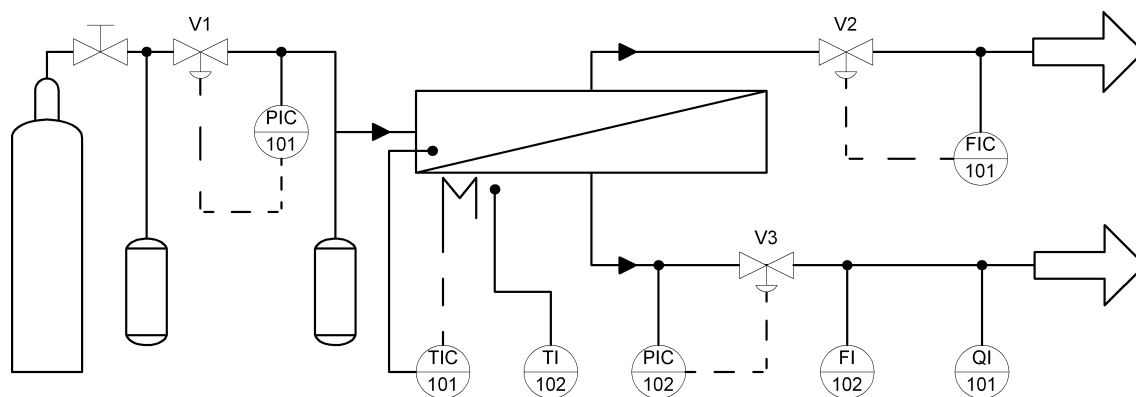


Figure 1. Schematic illustration of the setup.

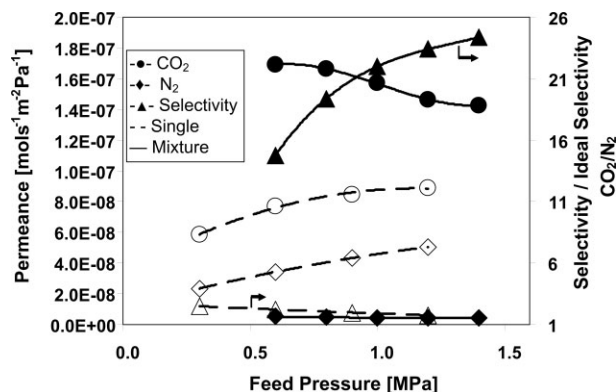


Figure 2. Permeance and selectivity of a binary mixture of CO₂/N₂ (20/80 mol.-%) as a function of feed pressure at a temperature of 293 K; \blacklozenge - N₂, \bullet - CO₂, \blacktriangle - selectivity. Additionally the permeance and ideal selectivity of single gases are presented (open symbols).

selectivity calculated from the single gas measurements is 2.1. Moreover, the decrease in selectivity with increasing pressure was expected according to prior single gas measurements. In contradiction to these results, a selectivity increase with increasing feed pressure was observed when working with real gas mixtures.

A similar permeation behavior is also reported by many authors, not only for microporous carbon membranes but also for zeolite-type membranes, especially for separation of gas mixtures with at least one strongly adsorbable gas [17–20]. Separation by these types of membranes occurs due to the selective adsorption-surface diffusion-desorption mechanism and is known in literature as selective surface flow [21]. More adsorbable components of the feed gas mixture are selectively adsorbed on the membrane pore walls at the high-pressure side, followed by their surface diffusion to the low-pressure side where they desorb to the low-pressure gas phase. In contrast, the transport of nonadsorbable components occurs in the gas phase of the pore. The activated diffusion, the Knudsen diffusion, or the viscous flow can dominate depending on the pore or the gas molecule size. In ultramicropores, the adsorbed molecules can hinder or completely block the flow of less- or nonadsorbable components of the feed gas mixture through the pore space. Furthermore, the transport through the pore membrane can be assumed in general as a coupled effect of surface flow and gas diffusion. One or the other effect dominates the transport through the membrane for different components, depending on the applied conditions or tested gas mixtures. The fluent transition between the effects is due to changing conditions [22].

The discrepancy between permeation of pure gases and mixed gases found in this study can probably be explained by competitive adsorption and diffusion of the different species in the membrane. Competitive adsorption means the competition of different components in the gas mixture for the same adsorption sites within the pores. This effect appears especially at higher pressure when the whole available pore surface is already occupied by adsorbed molecules. It is known from literature that the adsorbed amount of the component in the

mixture can be even larger than for the pure component [23]. The adsorption measurements of pure gases as well as of a binary mixture are necessary to determine the competitive adsorption. At the time of submission of this paper, adsorption data for the testing membrane and gas mixture were not available.

Contrary to competitive adsorption, the acquisition of competitive diffusion, i.e., interaction between adsorbed molecules and their transport along the pore surface, is more difficult, and it is a current research topic of many scientists [24, 25]. Several empirical equations are presented in literature [26]. However, they are not able to describe the phenomenon in its complexity. Using the Maxwell-Stefan theory it is possible to get a relatively good description of coupled gas and surface diffusion of a binary mixture with one adsorbable gas. It was less helpful for studying the behavior of mixtures consisting of already two adsorbable gases.

Both effects mentioned above could be the cause for the observed difference in the behavior of single gases and gas mixtures so that additional investigations are necessary to distinguish between them. The results emphasize that mixed gas adsorption and permeation measurements are required to define gas separation by means of the ultramicroporous membrane.

Summing up, it can be stated that the permeation of more adsorbable CO₂ through the tested carbon membrane occurs presumably by the adsorption-selective mechanism, whereas diffusion in the gas phase dominates the permeation of less adsorbable N₂. Due to the membrane pore size of approximately 0.34 nm and because of the mean free path of N₂ in the tested pressure and temperature range varying from 5 to 40 nm, Knudsen diffusion or activated diffusion can be expected. In order to distinguish between them, further investigations of permeance as a function of temperature are necessary, as they are presented in the following chapter.

The Robeson's upper bound and the tradeoff line between selectivity and permeability of polymeric membranes, which represent the current state-of-the-art technology in the area of polymeric materials for gas separation, and the tested carbon membrane for the CO₂/N₂ system are presented in Fig. 3. The thickness of the carbon separation layer (1 μ m, information from IKTS) was used to calculate the permeability (permeance \times membrane thickness) in [Barrer]. The single gas as well as the mixture gas measurement data are plotted in order to reflect the membrane performance precisely. In spite of the better membrane achievement for the gas mixture, the data point is below the upper bound, indicating further improvement demand for membrane performance.

3.2 Effect of Operating Temperature and Membrane Aging

The permeation behavior of both gases in the gas mixture through a new membrane as a function of temperature at a feed pressure of 1.4 MPa is presented in Fig. 4. Both the N₂ and the CO₂ permeance increase with increasing temperature, but the N₂ permeance increases stronger than that of CO₂, i.e., the

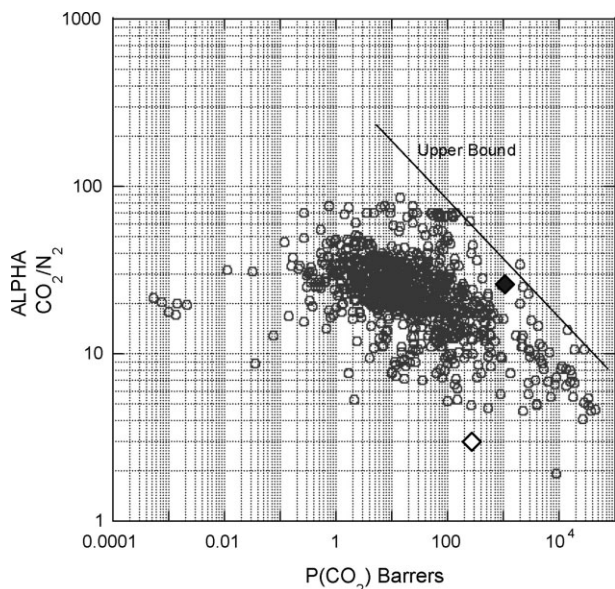


Figure 3. Revised Robeson plot for CO₂/N₂ [27]. The data point for the tested carbon membrane at the feed pressure of 1.2 MPa and temperature of 293 K is displayed for comparison for single gases (◇ open symbol) and gas mixture (◆ closed symbol).

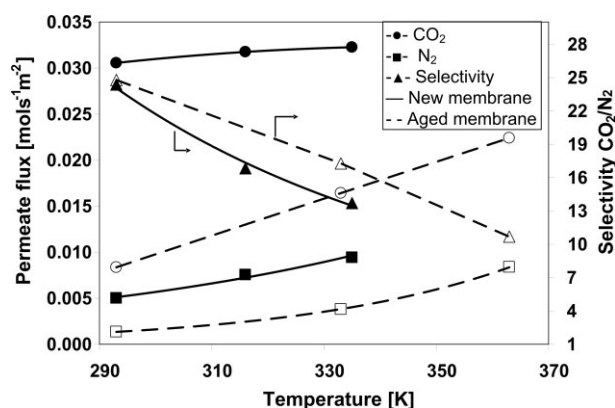


Figure 4. Permeate flux and selectivity of a binary mixture of CO₂/N₂ (20/80 mol.-%) as a function of temperature at a feed pressure of 1.4 MPa; ■- N₂, ●- CO₂, ▲- selectivity. Full symbols represent the values for a new membrane, open symbols denote the values for a membrane after permanent exposure to the gas mixture at 1.4 MPa.

selectivity decreases sharply with increasing temperature. At a typical power plant flue gas temperature of more than 363 K, the tested carbon membrane had a CO₂/N₂ selectivity of 10 and a CO₂ permeate flux of 0.022 mol s⁻¹ m⁻².

The observed permeation behavior of both components through the tested carbon membrane confirms the assumption of the dominating transport mechanism mentioned in the previous chapter. The fact that the N₂ permeance increases with increasing temperature leads to the conclusion that activated diffusion has a major effect on the total N₂ permeance. A decrease of permeance should appear in the case of Knudsen diffusion, but it was not observed in the current investigations.

For adsorbable gases like CO₂, the dependency on permeance as a function of temperature is known to occur as interplay of sorption capacity and surface mobility of adsorbed molecules. At low temperatures, the adsorbed capacity is high but the surface mobility of adsorbed molecules is quite low. With higher temperatures, the adsorbed capacity decreases but less than the mobility of the adsorbed molecules, so that the permeance increases initially and reaches a maximum at a certain temperature. With further increasing temperature, the permeance decreases due to the strong loss of adsorbed capacity. At this point, the diffusion in the gas phase of the pores begins to dominate the total transport through the membrane. Similar behavior was observed by many authors when investigating gas transport through microporous membranes [28–30].

Moreover, aging effects, defined as the change in membrane performance caused by time and environment, were observed. As demonstrated in Figs. 4 and 5, the membrane performance in terms of permeate flux decreases for both components after exposure of the membrane to the gas mixture at 1.4 MPa. Contrary to the permeate flux, the selectivity slightly increased in comparison to initial values.

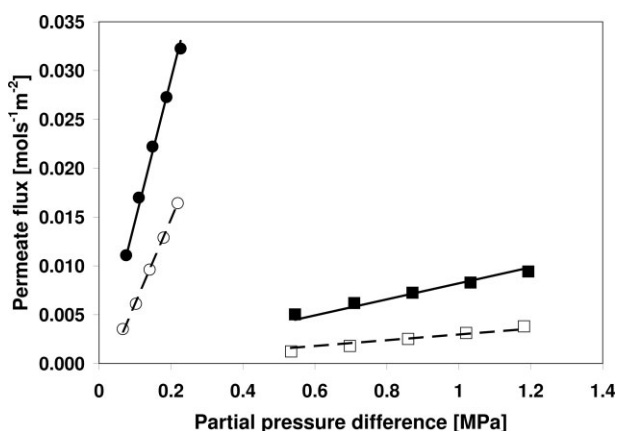


Figure 5. Permeate flux of binary mixture of CO₂/N₂ (20/80 mol.-%) as a function of partial pressure difference at 293 K; ■- N₂, ●- CO₂. Full symbols represent the values for a new membrane, open symbols denote the values for a membrane after permanent exposure to the gas mixture at 1.4 MPa.

Aging of carbon membranes is the topic of several studies published in literature [31, 32]. Reaction of oxygen from air with carbon, water vapor adsorption, and adsorption of easily condensable gases are the most-mentioned reasons for aging effects. As there was neither water vapor in the testing gas nor air contact between the experiments, strong adsorption of gas molecules in small pore constrictions causing pore blocking could be the reason for the observed membrane behavior in this study. Smaller molecules ($d_{k,CO_2} = 0.33$ nm) are hindered from diffusion as well but less than the larger ones ($d_{k,N_2} = 0.36$ nm), so that the selectivity increases. The discrepancy between a new and an aged membrane diminishes with increasing operating temperature, thus indicating the correctness of the adsorption assumption. Apart from the membrane

alteration due to adsorption, the partial pressure difference still remains the driving force for the process, as can be seen in Fig. 5.

4 Conclusions

The tested carbon membrane (IKTS, Hermsdorf, Germany) exhibits a good permeance and high selectivity for CO₂. The permeation experiments were conducted with single gases (CO₂, N₂) and a CO₂/N₂ gas mixture (20/80 mol.-%) at temperatures ranging from 293 K to 363 K and in a pressure range from 0.3 to 1.4 MPa. Permeation measurements revealed that the membranes are defect-free and have the potential for CO₂ capture in flue gas treatment. However, the membrane performance (permeance, selectivity) needs to be further improved in order to reach the economical industrial operation requirements. Additionally, the influence of water vapor and acid gases on the membrane performance as well as a long-term experiment to determine membrane stability and process efficiency remain subjects for further studies.

The selectivity of the binary mixture is much higher than the ideal selectivity, due to restricted diffusion of the less adsorbable N₂ and because of forced diffusion of the more adsorbable CO₂ in the binary mixture. Aging effects of the membrane caused by blocking of pore constrictions through adsorption were observed. Membrane-aging lowers the throughput, but apparently raises the selectivity. Operation at high temperatures leads to a reduction of aging effects.

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