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## Influence of separation temperature on the performance of adsorption-selective carbon membranes

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Gas separation by membranes has acquired a significant role in industry due to their economic competitiveness compared with the existing separation processes. At present, the major interest in membrane technology is focused on finding inorganic materials resistant to thermal and chemical influences and which have higher permeabilities and selectivities than polymeric membranes [1].

Carbon membranes have been identified as very promising candidates for gas separations as they present attractive properties for air separation, hydrogen recovery, olefin-paraffin separation, natural gas processing, hydrocarbon- $N_2$  separation, etc. [2]. However, their development at industrial scale requires a significant reduction in the current overall costs. This explains why, in recent years, research on carbon membrane technology has shifted towards the use of much lower-cost polymeric precursors and the simplification of manufacturing processes. Additionally, much attention has been paid to the selection of adequate operating conditions to achieve the optimal separation efficiency of carbon membranes.

Previous studies [3–5] have reported on the potential of phenolic resins as precursors of gas separation carbon membranes since a large variety of materials suitable for separation of different gas mixtures have been developed. Fuertes [4] has described the preparation of adsorption

selective-carbon membranes (ASCMs) from a phenolic resin following different processes which involved oxidation and carbonization steps. The resulting materials proved highly effective for recovery of hydrocarbons from gas mixtures formed by hydrocarbons and a nonadsorbable gas (i.e.  $N_2$ ,  $H_2$ , etc.) due to the selective adsorption of the hydrocarbons of the gas mixture onto the pore surface followed by the surface diffusion of the adsorbed molecule across the pore. On the other hand, the presence of adsorbed species significantly limited the diffusion of a nonadsorbable gas by reducing the size of accessible space through the pore. As a consequence, the separation process was highly selective and a hydrocarbon-rich gas was obtained as permeate stream.

Previous work [4] showed that a rise in the separation temperature from 25 to 150 °C produced a strong reduction in the separation factor as a consequence of the desorption of hydrocarbon molecules from the carbon membrane surface. The data suggested that a significant improvement of gas separation selectivity between adsorbable and nonadsorbable components may be achieved by working at temperatures below 25 °C. In order to clarify this point, the separation of gas mixtures containing adsorbable (i.e.  $C_1$ – $C_4$  hydrocarbons) and nonadsorbable components (i.e.  $N_2$ ) at temperatures in the range between –20 and 25 °C was examined in this work. In addition, the present study describes the preparation of an adsorption-selective carbon membrane by simple carbonization up to 700 °C of a phenolic-formaldehyde resin supported on a ceramic

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tubular support. The experimental results provided useful information to improve the separation properties of ASCMs.

The phenolic resin based-carbon membrane was formed by coating the inner face of porous ceramic tubes (US Filter, pore diameter=20 nm, 15 mm length×10 mm O.D.×7 mm I.D.) with a Novolak-type phenolic resin film and subsequent heat treatment under vacuum (<0.01 mbar) up to 700 °C (heating rate=1 °C/min). The sample was held at the maximum temperature for 1 h. Permeation tests at temperatures between -20 and 25 °C were carried out with binary gas mixtures containing C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub> or *n*-C<sub>4</sub>H<sub>10</sub> and N<sub>2</sub> (hydrocarbon–N<sub>2</sub>, 50:50, v/v). The performance of the membrane for separation of multi-component gas mixtures was also analyzed by using mixtures A (20.4% CH<sub>4</sub>, 20.1% C<sub>2</sub>H<sub>6</sub>, 20.3% C<sub>3</sub>H<sub>8</sub>, 39.2% N<sub>2</sub>) and B (18.4% CH<sub>4</sub>, 18.1% C<sub>2</sub>H<sub>6</sub>, 18.3% C<sub>3</sub>H<sub>8</sub>, 10% *n*-C<sub>4</sub>H<sub>10</sub>, 35.3% N<sub>2</sub>). The gas mixture was introduced at 1 bar into the inner side of the tubular membrane whereas He flowed through the permeate side (1 bar). The gas concentration in the permeate side was evaluated by a Hewlett-Packard TCD-GC. The experimental procedures have already been described in detail elsewhere [4].

The important effect of adsorption processes on the carbon membrane performance for separation of binary gas mixtures (hydrocarbon–N<sub>2</sub>) is illustrated in Fig. 1. For the C<sub>2</sub>H<sub>4</sub>–N<sub>2</sub> mixture, the low adsorption coverage of C<sub>2</sub>H<sub>4</sub> slightly affected the transport of N<sub>2</sub> through the pores, which took place mainly by gas diffusion. The reduction observed in N<sub>2</sub> permeability from 347 Barrer at 25 °C to 174 Barrer at -20 °C was mainly related to the decrease in

Table 1

Effect of temperature on selectivity (hydrocarbon–N<sub>2</sub>) through a phenolic resin derived-carbon membrane for binary mixtures (hydrocarbon–N<sub>2</sub>, 50:50, v/v)

| Temperature (°C) | Selectivity                                   |   |  |
|------------------|---|---|--|
|                  | C <sub>2</sub> H <sub>4</sub> –N <sub>2</sub> | C <sub>3</sub> H <sub>6</sub> –N <sub>2</sub> | <i>n</i> -C <sub>4</sub> H <sub>10</sub> –N <sub>2</sub> |
| 25               | 3.8   | 22.8  | 89   |
| 0                | 5.3   | 33.6  | 257  |
| -10              | 6.3   | 51.0  | 186  |
| -20              | 7.4   | 67.3  | –  |

gas diffusivity of N<sub>2</sub>. However, the decrease in N<sub>2</sub> permeability with temperature was more pronounced as the hydrocarbon condensability increased from ethylene to *n*-butane. According to Yang et al. [6], the presence of adsorbed molecules creates a potential barrier and the transport of N<sub>2</sub> through the membrane followed the expression:

$$F_g^* = F_g e^{-(E_o\theta)/RT} \quad (1)$$

where  $F_g$  is the permeability of the pure N<sub>2</sub>,  $\theta$  the surface fraction covered by the adsorbed species and  $E_o$  the potential barrier introduced at  $\theta=1$ . As deduced from Eq. (1), the permeability of N<sub>2</sub> was reduced as the hydrocarbon of the mixture established higher potential barriers ( $E_o\theta$ ) to its diffusion through the pores of the membrane. That explains the limited N<sub>2</sub> flow (59.6 Barrer at 25 °C) in the presence of C<sub>3</sub>H<sub>6</sub> (weakly adsorbing-hydrocarbon) and the drop of N<sub>2</sub> permeability to 15 Barrer at 25 °C for the

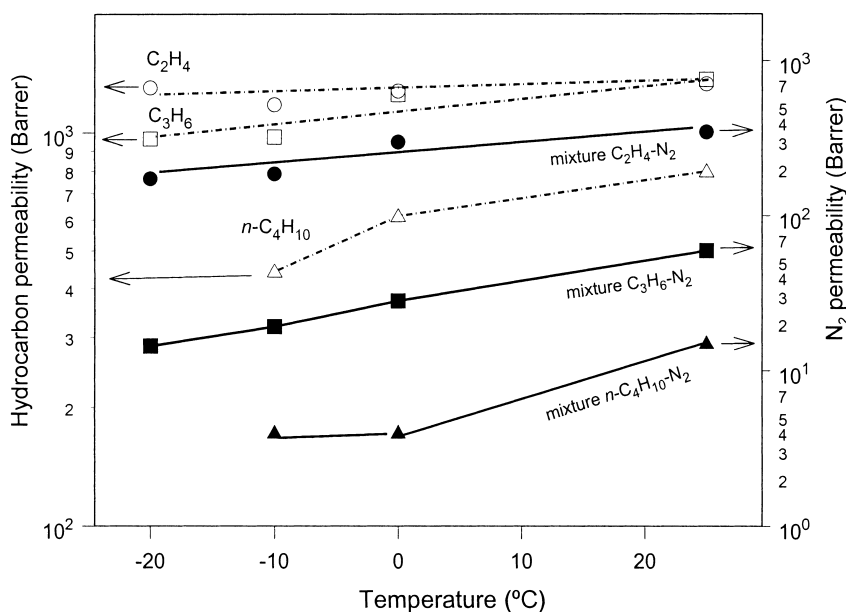


Fig. 1. Modification of gas permeability through phenolic resin derived-carbon membrane with temperature; binary gas mixtures (hydrocarbon–N<sub>2</sub>, 50:50, v/v).

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