Novel carbon molecular sieve honeycomb membrane module: configuration and membrane characterization

S. Lagorssea, A. Leitea, F.D. Magalhãesa, N. Bischofbergerb, J. Rathenowb, A. Mendesa,*

a LEPAE, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Roberto Frias, 4200-465 Porto, Portugal
b Blue Membranes GmbH, Rheingaustr. 190-196, D-65203 Wiesbaden

Received 25 August 2004; accepted 4 November 2004
Available online 21 December 2004

Abstract

A new production concept of carbon molecular sieve membranes modules is described. The supported membrane synthesis process allows for industrial production with uniform and reproducible properties, using flat membranes as a starting precursor. The corresponding membrane modules are made in a honeycomb configuration, leading to high packing density and thermochemical stability. Some of the carbon membranes produced for use in these modules are characterized. Species H2, O2, N2, CO2 and SF6 were used in monocomponent adsorption and permeation experiments to obtain adsorption equilibrium and permeation data. High permeabilities were attained in combination with high selectivities. The pore size distribution of the membrane was determined. A number of complementary morphological and structural characterizations were also performed.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: A. Molecular sieve; B. Heat treatment; C. Adsorption; D. Porosity, Transport properties

1. Introduction

The development of membrane processes for the separation of gas mixtures has shown considerable evolution in the last two decades [1]. Polymeric membrane processes are currently being used on a large scale for: recovery of hydrogen from purge gas and hydrocarbon streams, adjustment of H2/CO2 ratio in syngas, removal of CO2 from natural gas, recovery of helium, drying of gas streams and air separation [1–4].

Industrial implementations of carbon molecular sieve membranes (CMSM), also known as nanoporous carbon membranes, have been long awaited in the gas separation field, due to their promising high performance [5–7]. Indeed, compared to the polymeric membranes, CMSM are simultaneously more selective and permeable, are thermochemically more stable and, most interestingly, allow for the possibility of fine-tuning the pore size [8].

Some of the potential applications where CMSM can contribute with significant performance gains include carbon dioxide separation from bio- and natural gas [9], production of nitrogen or oxygen from air [10], separation of hydrocarbons having similar boiling points [11] and purification of hydrogen from steam reforming [7].

Koresh and Soffer pioneered the development of CMSM for gas separation processes [12,13]. This application was patented in 1987 by Soffer et al. [14]. A few years later the same author co-authored some other related patents [15–17]. These patents ended up being
bought by an Israeli company named Carbon Membranes Ltd. A number of studies have since followed. Along the last few years, much of the literature on CMSM has been mainly focused on membrane synthesis, aiming at obtaining improved gas separation performances. Preparation of CMSM has followed two distinct routes: (1) either through the carbonization of a preexisting polymeric substrate (hollow fibers, self-supporting thin polymeric film) or (2) through the carbonization of films deposited on underlying macro- and mesoporous supports (to improve mechanical stability of the carbonized films). Several precursors have been used such as polyimide, polyacrylonitrile (PAN), phenolic resin, cellulose [5], and, recently, ultrafiltration fiber membranes [18]. There have also been reported, by Koros and co-workers, composite carbon membranes (aiming at reducing adverse humidity effects) [19] and, more recently, mixed matrix membranes (using CMS particles to counter the costly processing of purely homogeneous CMSM) [20–23]. A more detailed review of the carbon membranes developed until 2001 can be found in a paper by Ismail and David [6]. Recently, Saufi and Ismail published a review on the fabrication aspects of these membranes [5].

Some works have studied some other important issues related to CMSM. These include the stability of the membranes toward air oxidation and humidity [24,25], membrane regeneration and conditioning strategies [26,27] and characterization of gas transport [28–31]. Fundamental understanding of the microporous structure of these materials is still difficult. Unlike well-crystallized materials, carbon molecular sieve membranes are randomly structured and, depending on the precursor and the production process, they possess variable pore size distribution. Only a few studies have attempted to characterize and model the porosity of these materials [32].

Membrane module construction is seldom referred in literature. To date, only tubular and hollow fiber testing modules (lab-scale modules) have been constructed using carbon membranes [31,33,34]. The industrial use of these materials has been impaired by difficulties in obtaining, in large-scale production lines, large membranes showing reproducible structure and absence of defects. Their assembly in high packing density modules has also been difficult and is affected by the poor mechanical stability of the materials. To our knowledge, the assembly of large CMSM modules has only been described by Soffer et al. [14,16,17]. The only successful industrial production high-quality CMSM modules was achieved by Carbon Membranes Ltd (Israel), with a hollow fiber configuration [31]. But the company closed in 2001 and no such units are commercially available today.

In an attempt to overcome the gap between research and commercialization, Blue Membranes GmbH (Germany) is developing a new concept of carbon molecular sieve membrane module for gas separation: the honeycomb membrane module configuration (HM). This new module design will be a competitor to the well-
known hollow fiber configuration, found in commercial polymeric membrane modules.

The present paper describes recent work on CMSM development, in an effort to make viable the use of these materials in industrial applications. The new honeycomb CMSM module configuration is presented. The membrane synthesis is part of the whole module manufacture process. The performances achieved with the developed membranes are also reported, together with structural characterization results, namely concerning the pore size distribution using the model proposed by Nguyen et al. for carbon materials [35].

2. Honeycomb CMSM module

The success of a membrane separation system does not depend only on the separation performance of the membrane material. The module itself must offer a reliable and efficient operation and its manufacture must be feasible and economical in an industrial scale. Nowadays, a number of module designs can be found, based on two types of membrane configuration: flat or tubular. The choice of a particular module is determined by the type of application and economic considerations. The hollow fiber membrane module is, up to now, the configuration that yields the highest packing density. To our knowledge, Carbon Membranes Ltd obtained, using this configuration, the highest packing density reported for CMSM modules: about 2000 m² m⁻³ (10000 fibers and 4 m² per module).

The new membrane module design, constructed from a flat membrane precursor, which particular configuration originates its designation as “honeycomb module” [36], is described next. It possesses a high packing density (up to 2500 m²/m⁻³ and 10 m² per module). The flat supported membrane is produced using industrially common techniques. The support is an industrial grade paper modified with ceramic fibers. This material, being distinct from the usually employed ceramic supports, limits differential shrinking during pyrolysis of the support and precursor layers, therefore avoiding residual stresses that would affect the membrane’s mechanical stability. This support is then sheeted with a polymeric film (that constitutes the precursor of the membrane’s carbon molecular sieve layer—the selective layer) using an imprinting technique. This process allows for fully automated industrial production. The precursor selection is quite important for the final membrane performance: the pores of the selective layer will vary in size, shape and degree of connectivity depending on the morphology of the organic precursor and the chemistry of its pyrolysis. A mixed polymer system composed of a phenolic resin (a commercially available resol type—Phenodur PR 515) and of an epoxy resin (Beckopox EP309) was used. Phenolic-resin-derived activated carbon was described by Tennison [37]. For the coating procedure, resins were dissolved in methyl ethyl ketone.

The final honeycomb module configuration is obtained starting from this flat precursor sheet (Fig. 1), even before any pyrolysis treatment. First, a corrugated sheet is obtained using a stamping procedure (Fig. 1a). The wavy pattern has a diagonal orientation in relation to the sheet’s length direction. Next, the sheet is pleated (Fig. 1b). By overlapping the pleated corrugated segments, flow channels in cross-flow directions are obtained without the need for a spacer material. The permeate and feed sides become independent by sealing,

---

Fig. 1. Schematic of the honeycomb CMSM module preparation procedure: (a) flat corrugated precursor; (b) pleated precursor; (c) membrane module.
at the edges, those alternate sets of layers on which the polymeric film layers face each other (Fig. 1c). This creates pocket-like chambers that will constitute the permeate side of the module. By taking advantage of the thermosetting properties of the polymeric layer, a strong bond at the contacting edge is obtained. This is done in a cure stage at moderate temperature.

The subsequent pyrolysis step turns the polymeric precursor into a cross-linked porous network of amorphous carbon material, which mean pore size can be tailored by controlling the temperature and duration of the treatment. Pyrolysis is done under inert atmosphere using nitrogen. The membrane is heated up to 1053 K with a heating rate inferior to 1 K min\(^{-1}\). The maximum temperature is held for 3 h, after which the membrane was allowed to cool down to ambient temperature.

Finally, fine-tuning of the molecular sieving properties is obtained through a carbon vapor deposition (CVD) process, followed by an activation step. The vapor deposition of pyrolytic carbon, obtained from an organic source, leads to the overall blockage of the existing pore system (hydrocarbon cracking). To accomplish that, the membrane is heated in a quartz tube furnace under inert atmosphere (using nitrogen) up to 923 K at a rate of 10 K min\(^{-1}\). At this temperature, the membrane is brought in contact with propylene for 1 min. Before allowing the sample to cool down, nitrogen was used to purge the system. A similar CVD procedure was described by Hayashi et al. [38].

Through a controlled oxidation process (activation step) as described by Fuertes and Menendez [39], using air at a temperature ranging from 523 to 623 K and for times ranging from 1 to 3 h, the pores are then re-opened, leading to a pore size distribution that is narrower than the previous one (before CVD). This final procedure (CVD + activation) allows both for the improvement of the membrane’s intended selectivity and for the repair of defects that might be present in the original pyrolysed layer. Note that the CVD/activation is one of the possible strategies for pore adjustment. The support layer maintains a meso/macroporous structure. After the heat treatments, the module is sealed into a housing. Fig. 2 summarizes the production steps involved in the fabrication of a honeycomb CMSM module. Further improvements are being done, namely the optimization of the housing step and of the mass transfer efficiency.

Fig. 3 shows two scanning electron microscopy (SEM) pictures of a cross-section of a membrane synthesized at Blue Membranes. The corrugated shape is quite evident in Fig. 3a. Two layers can be distinguished (Fig. 3b): the meso/macroporous support layer and the selective layer. The total thickness of the membranes produced is around 50–100 μm while the ultramicroporous carbon layers have an average thickness between 10 and 30 μm. SEM pictures obtained also show consistently that the selective film has an apparently dense, crack-free, structure.

Samples of some carbon membranes produced by the method described above were tested and characterized as described next.

3. Membrane characterization

3.1. Experimental procedures and apparatus

For the permeation and equilibrium sorption measurements, different gases were selected: H\(_2\), CO\(_2\), O\(_2\), N\(_2\) and SF\(_6\).

Monocomponent gas permeabilities were obtained in a thermostabilized permeation apparatus. The system consisted of a 33 cm\(^2\) flat sheet cell in which the pressure gradient was generated both by pressurizing the feed and by evacuating the permeate side of the membrane. The feed and permeate pressure were read using pressure transducers (Druck, model PMP 4010, accuracy ± 0.04%). The feed was high-purity gas supplied directly from compressed gas cylinders. The feed pressure was controlled with a pressure regulator (Joucomatic,
0–4 bar) placed after the two-stage pressure regulator on the cylinder. The permeation flux through the membrane was determined either by monitoring the increase in permeate pressure on a calibrated volume or by measuring the mass flow rate of the permeating species (Bronkhorst HI-TEC flowmeters, chosen in accordance with the flowrate range). The pressure transducers and the flowmeters were logged directly into a computer (by Labview). An electronic micrometer was also used to measure the total thickness of each membrane tested, a value of 108 μm were usually obtained.

Pure component adsorption equilibrium isotherms were determined using a volumetric type apparatus. Internal volumes of the system were accurately calibrated. In the experimental runs, the temperature of the sample was monitored with a thermocouple and the evolution of the gas phase pressure was measured with a high accuracy pressure transducer (Druck, model PMP 4010, accuracy ± 0.04%). Between experiments the CMSM sample was degassed until a constant pressure of 0.006 bar at 343 K. The sample consisted of about 2 g of broken-up flat membranes.

Several other characterization techniques were used on the membranes. These includes He pycnometry, mercury porosimetry and CO₂ adsorption data. The mercury porosimeter detects pores in the range of 3.5 nm to 10 μm. Adsorption equilibrium data were also used to estimate the micropore size distribution and the microporosity.

### 3.2. Single gas permeation

CMSM single gas permeabilities were measured at 303 K and at a feed pressure of 2 bar while the permeate pressure was kept below 1 bar. The “permeability”, $P$, of the membrane towards a species was determined as described by the following equation:

$$ P = \frac{\text{Flux}}{\Delta p/\ell} $$

(1)

where $\Delta p$ is the partial pressure difference of the species across the membrane and $\ell$ is the thickness of the membrane. For convenience, one also uses the permeance or mass transfer coefficient, $k_p$, defined as:

$$ k_p = \frac{P}{\ell} = \frac{\text{Flux}}{\Delta p} $$

(2)

Table 1 shows the performances of some of the membranes produced according to the synthesis strategy described above. All samples were pyrolysed under the same conditions; the differences are related to the final activation step. Samples A were activated for a period two times longer than samples B. Samples A1 and B1 correspond to the highest temperature used during the activation step, while B3 and A2 were submitted to the lowest activation temperature.

An increase in the activation temperature opens the pore slightly which affects the diffusivities of the species in a different way according to their sizes. Permeabilities of group B towards O₂, CO₂ and N₂ show an increase of 141%, 150% and 203%, respectively, while an increase of only 85% toward H₂ is observed, when moving from sample B3 to B1. As expected, the activation step performed a more pronounced effect on the diffusivity of the larger species. Consequently, the ideal selectivities decrease generally with increasing activation temperature.

Both the temperature and duration of the activation step have a significant effect on the performance of the carbon membranes. These effects being reproducible, the synthesis conditions can be appropriately controlled in order to tune the desired separation properties.

The monocomponent permeabilities obtained indicate good membrane performances (high permeabilities were attained in combination with high selectivities).
when compared to the literature data. Shiflett and Foley [40] reported a very high $O_2/N_2$ ideal selectivity ($O_2/N_2 = 30.5$) in a CMSM, but very low permeabilities. In such case, the mean ultramicropore size should have been very close to the effective molecular diameter, making this separation very close to the true molecular sieving for these species. Jones and Koros [41], in a single fiber module, obtained quite high permeabilities and good selectivities, in the order of some of the results shown here. Also noteworthy is the work of Gavalas and co-workers [42], for tubular supported carbon membranes, showing good performances for $H_2$ and $CO_2$ separation. It must be noted, however, that the works cited are reported to lab-scale production of small area membranes and do not attempt to address the problem of reproducible and reliable assembly of large membrane modules.

3.3. Adsorption equilibrium

The adsorption equilibrium isotherms for $H_2$, $N_2$, $O_2$ and $CO_2$ at 303 K up to 8 bar on sample B2 are represented graphically in Fig. 4. Fig. 5 shows the adsorption equilibrium isotherms for $N_2$ and $CO_2$ at three different temperatures.

The obtained isotherms are favourable (type I) and, in the case of $H_2$, $N_2$ and $O_2$, the equilibrium points were fitted to a Langmuir equation. Both $N_2$ and $O_2$ are relatively weakly adsorbed and the isotherms are very close. For $CO_2$, equilibrium data were fitted using the UNILAN equation. Even though good fittings are also obtained with Langmuir–Freundlich or Dubinin–Radushkevitch equations, these do not tend to a Henry equation limit at low pressure and are, therefore, thermodynamically inconsistent. The fitted isotherm equations parameters are summarized in Table 2.

The samples were also probed using $SF_6$. No adsorption was detected up to 5 bar. Beyond the limit of true molecular sieving, when the ratio of pore diameter and effective molecular diameter becomes smaller than unity,
repulsive forces in the potential field become dominant. Accordingly, the sorption energy becomes smaller and finally the molecule is not allowed to stay in the micro-porous system. Consequently, the adsorption experiments would ideally show no uptake of the sieved component. This is the case of SF$_6$, which is used to detect membrane defects, like cracks, in CMSM.

The adsorption equilibrium data are useful to obtain information concerning the CMSM structure at the microporous level, as described in the next two sections.

3.4. Structural characterization

Different techniques have been used to characterize the porous structure of the CMSM produced. Some results obtained for sample B2 are presented next.

An average skeleton density, $d_{\text{He}}$, of 1.977 g/cm$^3$ was determined by helium pycnometry. The mass fraction of the ceramic portion of the support was obtained by thermogravimetric (TG) analysis; a value of 0.40 was obtained. Using this value together with the average skeleton density, one obtains a carbon matrix density, $d_c$, around 1.704 g/cm$^3$, which is significantly lower than the density of pure graphite (2.3 g/cm$^3$).

The Dubinin method was employed to estimate the micropore volume using CO$_2$ adsorption data at 273 K [46]. The corresponding characteristic curve given in Fig. 6 is quite linear, indicating that the Dubinin–Radushkevitch (DR) equation provides a reasonable description of the adsorption equilibrium at this temperature. The fitting parameters of the DR equation are $E_0 = 32.7$ J mol$^{-1}$ and $q_1 = 2.42$ mol kg$^{-1}$. Considering a density for the adsorbed CO$_2$ of 0.96 g/cm$^3$, as proposed by Cazorla-Amarós et al. [47], a micropore volume, $V_{l_p}$, of 0.110 cm$^3$/g was determined. Table 3 summarizes all these results together with some published data [31,48]. The specific micropore volume determined is approximately two or three times lower than the published data. This is expected since the pore volume was calculated per unit membrane mass (support and microporous carbon layer). In the published data the volume is referred to the mass of microporous layer alone. Considering the mass fraction of carbon in the membrane, the specific micropore volume will be:

$$V_{l_p} = \frac{V_{l_p}}{0.6},$$

leading to 0.35 cm$^3$/g. This value agrees with the published data presented in Table 3.

Also shown in Table 3, is the average micropore width of the slit-shaped micropores, $L_0$, estimated using the simple approach proposed by Stoeckli et al. [49]:

$$L_0 (\text{nm}) = 10800 (\text{nm J mol}^{-1})/(E_0 - 11400 (\text{J mol}^{-1}))$$

The result obtained with this approximation is $L_0 = 0.51$ nm. This value will be compared, in next section, to the one found from pore size distribution.
3.5. Pore size distribution

Recently, Nguyen and Do [50,51] proposed a method for the determination of micro- and mesopore size distribution in carbonaceous materials. This method accounts for the enhancement of the potential energy of interaction between adsorbate molecules and the atoms within the pore’s walls. The Langmuir isotherm is used to describe the adsorption behavior inside the pores. The key concept consists in admitting that there is a different isotherm for each pore size (single pore isotherm), i.e., the parameters of the isotherm are a function of the pore size. For the Langmuir isotherm, the fractional coverage, $\theta$, becomes [50]:

$$\theta(r) = \frac{q(r)}{q_m(r)} = \frac{b_{pore}(r)p_{pore}(r)}{1 + b_{pore}(r)p_{pore}(r)}$$

where parameter $b_{pore}(r)$ is estimated as a function of the heat of adsorption inside the pore and is a function of temperature; the pressure inside the pore is related to the bulk pressure and to the potential energy of the molecules in the gas phase inside the pores. Slit shape geometry is assumed for the pores. The total potential energy is the summation of the potential energy due to the two opposite pore walls. The potential of a molecule relative to a flat surface is calculated by the Steele equation, also known as the 10-4-3 Steele potential [52,53]:

$$H(z) = 2\pi\rho_s\epsilon_{sf}\sigma_{sf}^4\left[\frac{2}{3}\left(\frac{\sigma_{sf}}{z}\right)^{10} - \left(\frac{\sigma_{sf}}{z}\right)^{4} - \frac{\sigma_{sf}^4}{3A(0.61A + z)^3}\right]$$

where $z$ is the distance relative to the flat surface. The equation’s parameters are: $\rho_s$—density of graphite, $A$—distance between two successive graphite layers, $\epsilon_{sf}$—interaction energy solid–fluid and $\sigma_{sf}$ the geometrical parameter of interaction solid–fluid (collision diameter). The last two parameters are also known as the Lennard-Jones potential parameters.

Once one has an isotherm for each pore size, the pore size distribution can be estimated, so that the model equation fits the experimental data [54]:

$$\theta_{exp}(p) = \int_{r_{min}}^{r_{max}} \theta_{calc}(p, r)f(r)\,dr$$

where the pore size distribution function, $f(r)$, is such that:

$$\sum_{i=1}^{n} f(r_i) = 1$$

The CO$_2$ adsorption equilibrium data on sample B2 at three different sub-critical temperatures (273, 275 and 303 K) were considered. The adsorption data used are shown in Fig. 7, together with the fitting curves derived from the Nguyen and Do method.

Fig. 8 gives the pore size distribution for the sample B2. The results show an extremely narrow size distribution in the ultramicropore range that provides the high sieving effect evidenced by the tested membranes (see Table 1). About 91.6% in volume of the ultramicropores are in the range of 0.60–0.68 nm and about 7.3% are in the range of 0.36–0.44 nm. An effective average pore diameter of 0.62 nm was computed from the distribution. This value is slightly higher than the one obtained using Stoeckli approach (0.51 nm), mentioned in the previous section. It should be noted that, the pore sizes were calculated from the distance between the centers of

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dubinin approach $V_m$ (cm$^3$ g$^{-1}$)</th>
<th>Dubinin approach $E_0$ (kJ mol$^{-1}$)</th>
<th>Stoeckli approach $L_0$ (nm)</th>
<th>Stoeckli approach $d_s$ (g cm$^{-3}$)</th>
<th>Micropore size (Å)</th>
<th>L Cm</th>
<th>Pycnometry and TG $d_m$ (g cm$^{-3}$)</th>
<th>Mercury porosimetry $d_{ap}$ (g cm$^{-3}$)</th>
<th>$V_{total}$ (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMSM</td>
<td>0.110$^a$</td>
<td>32.7</td>
<td>0.49–0.68</td>
<td>0.51</td>
<td>1.704</td>
<td>0.31</td>
<td>0.15</td>
<td>0.142$^a$</td>
<td>1.062$^a$</td>
</tr>
<tr>
<td>Published data</td>
<td>CMST3A [48]</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CMSM1 [31]</td>
<td>0.28</td>
<td>31.6</td>
<td>0.55</td>
<td></td>
<td></td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Pore volumes are per unit membrane mass (support and carbon layer).
the carbon atoms in opposite walls. So, one had to account for half a carbon atom on each wall (diameter of a carbon atom is 0.34 nm [51]).

This apparently bimodal distribution may provide the first experimental evidence of the long ago proposed model of the CMSM pore system: an ultramicroporous network comprised of “wide” segments (“cavities”) randomly interrupted by short constrictions [12]. The latter provide the molecular sieving performance (selectivity), but, since they constitute a small fraction of a species’ diffusional path across the membrane, relatively high permeabilities can still be obtained. The cavities additionally contribute to increase the membrane’s adsorption capacity.

The sieving character of the constrictions is evidenced when the membrane is probed with SF₆ and Xe (having molecular sizes, based on liquid molar volume, of 0.502 and 0.39 nm respectively [55]). Adsorption experiments showed no uptake of SF₆ up to 5 bar (see Section 3.3), while there is a very slow xenon uptake. Attending to the molecular sizes of both species, these results are coherent with the ND estimation for the pore size of the constrictions (0.36–0.44 nm).

Mercury porosimetry was used to determine the pore size distribution of the meso/macroporous support, in the range of 3.5 nm to 10 µm. An apparent density, \( d_{\text{ap}} \), of 1.062 g/cm\(^3\) and a void fraction, \( p_{\text{M/M}} \), of 31.2% were determined by this technique. An average pore size of 3.11 µm was determined for the pore size distribution of the support.

If one assumes that the void fraction obtained with the mercury porosimeter is only due to the meso/macroporosity of the support, some interesting values can be taken from this technique and its combination with helium pycnometry (skeleton density, \( d_{\text{He}} \), of 1.977 g/cm\(^3\)). The total pore volume can be obtained from the skeleton density, \( d_{\text{He}} \), and the apparent density, \( d_{\text{ap}} \) (\( V_{\text{total}} = 1/d_{\text{ap}} - 1/d_{\text{He}} \)) and gives 0.436 cm\(^3\)/g. From Eq. (8),

\[
\frac{V_{\text{pores} < 3.5}}{V_{\text{total}}} + \frac{V_{\text{pores} < 3.5}}{V_{\text{total}}} + \frac{V_{\text{solid}}}{V_{\text{total}}} = p_{\text{M/M}} + V_{\text{pores} < 3.5} \frac{d_{\text{ap}}}{d_{\text{He}}} = 1
\]

one can estimate, for pores up to 3.5 nm, a porosity of 15.1% and a volume, \( V_{\text{pores} < 3.5} \), of 0.142 cm\(^3\)/g, which is close to the one obtained from Dubinin method of 0.110 cm\(^3\)/g. All these values are listed in Table 3.

Combining the information obtained from Nguyen and Do method and from mercury porosimetry, one obtains the overall pore size distribution of the membrane, as shown in Fig. 9.

4. Conclusions

This work presents some valuable advances towards making CMSM modules available for industrial use. The honeycomb module configuration, together with the good gas separation performances exhibited by the synthesized membranes, seems to constitute a strong candidate to the long awaited use of CMSM in gas separation processes.

The advantages of the honeycomb membrane module, compared to traditional modules, are the high packing density and the self-supporting structure despite using flat membranes as a starting precursor. This new assembly concept also avoids the problems caused by the typically high brittleness of CMSM, since the membrane precursor is shaped into its final configuration prior to the application of any heat treatment.

Several membrane samples taken from the production process described above were characterized, having different pore fine-tuning procedures. The monocomponent permeability experiments revealed good membrane...
performance: high permeabilities were attained in combination with high selectivities. Adsorption equilibrium isotherms were also obtained. For carbon dioxide, the equilibrium data were fitted to the UNILAN equation, whereas the Langmuir equation was used for H₂, N₂ and O₂.

For the first time, the method developed by Nguyen and Do was applied to CMSM, yielding a narrow ultramicropore size distribution with an average pore size around 0.63 nm. The combination of Nguyen and Do and mercury porosimetry methods allowed for the determination of the overall pore size distribution of the membrane (support + selective layer).

The pore size distribution obtained provides evidence of a meso- and macroporous support combined with an ultramicroporous structure comprised of constrictions intercalating larger diameters segments.

Acknowledgements

The authors gratefully acknowledge the financial support from European Growth Project GRD1-2001-40257-Spec Sep and FCT research project POCTI/EQU/34224/2000.

References


