



# Helium and hydrogen selective carbon hollow fiber membranes: The effect of pyrolysis isothermal time



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## ABSTRACT

In the present study carbon molecular sieve (CMS) hollow fiber membranes have been produced by using P84 co-polyimide as precursor material and Argon as inert gas at three different pyrolysis procedures. Specifically, the pyrolysis conditions varied in terms of isothermal time (5, 30 and 60 min) at a final pyrolysis temperature of 1173 K. The pure gas permeance measurements of He, H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> purge gases were carried out for all produced carbon hollow fiber membranes (CHFMs) at 333 K. Results show that a longer isothermal time (or the maintenance time) on the higher temperatures results in more selective but less productive CMS membranes. The produced carbon hollow fiber membranes present very high permselectivity values, especially for helium and hydrogen gaseous mixtures. In fact, the maximum ideal selectivity values obtained for He/CH<sub>4</sub>, H<sub>2</sub>/CH<sub>4</sub>, He/N<sub>2</sub> and H<sub>2</sub>/N<sub>2</sub> gas couples were up to 2925, 5500, 350 and 600 respectively. Furthermore, gas mixture experiments present higher selectivity values than the corresponding calculated.

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## 1. Introduction

Porous materials have gained an important place in chemical technology and are used in a broad range of applications. Due to their high efficiency, simple operation and low, capital and operating cost, porous carbon membranes have been proposed as possible candidates for industrial scale separations of gaseous mixtures.

Historically, the development of porous inorganic membranes goes back to the 1940s decade, long before the discovery of today's synthetic organic membranes [1]. These first membranes were made and used primarily for the uranium isotopes separation, a project focused on military purposes [2,3]. Since then, several research groups worldwide have developed novel methodologies and new membrane materials as it is depicted by the vast number of research papers and patents with the purpose to transmit knowledge from the lab to the industry in order to fill the so called

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innovation gap. In particular, a plurality of new promising membrane materials such as block, di-block and tri-block, copolymer membranes [4–6], miscible glassy polymers [7], zeolite membranes [8–10], AIPO membranes [11,12], mixed matrix membranes (MMMs) [13–16], carbon molecular sieve membranes [17–19], ceramic membranes [20–22], and silica membranes [23–25] are reported in the literature. Among all these types of membranes carbon membranes are traditionally one of the most promising candidates for gas separations, thanks to their easy way in the preparation routes, the plurality of the precursor choosing, the ability in the enhancement of the properties of the final structure and of course because of the big experience of the scientific community on the topic [26–28].

Carbon membranes can be produced by pyrolysis of a variety of carbon-containing materials, under vacuum or inert atmosphere [1,29,30]. Typical polymeric precursors are various types of polyimides, polyacrylonitriles, polyfurfuryl alcohol, polyvinylidene chloride-acrylate terpolymer (PVDC-AC), phenol, formaldehyde and cellulose while the temperature of the pyrolysis step ranges between 400 and 1200 °C, under either inert or reactive environment [1,14,17,29,31,32]. Among them, the polyimides are one of the most promising materials as candidates for the production of conventional polymeric membranes [33–36]. Polyimide mem-

branes can be further used as precursors for the development of stable nanoporous carbon membranes that exhibit satisfactory permeability and selectivity properties [37].

Carbon membranes can find potential applications in the purification of H<sub>2</sub>, separation of olefin/paraffin mixtures, CO<sub>2</sub> recovery from natural gas, enrichment of syngas, water treatment processes and production of oxygen [26,29,38,39]. On the other hand, research work for the utilization of carbon membranes for helium separations is very limited [40]. For this kind of separations super-microporous structures, such as molecular sieve membranes are requested.

However, thorough knowledge of the factors affecting both membrane micro structure and gas permeation properties during the pyrolysis step is essential for the manufacturing tailor made and highly efficient membranes. To this end, in the case of carbon molecular sieves membranes, the ability to fine tune the pore size during the pyrolysis process is the major milestone of researchers who are working in this field.

In 1994 Jones and Koros produced carbon molecular sieve gas separation membranes by pyrolyzing various thermosetting polymeric materials under a variety of pyrolysis conditions. They found that the lower temperature protocol yielded membranes with O<sub>2</sub>/N<sub>2</sub> selectivities ranging from 8.5 to 11.5 while a higher temperature pyrolysis yielded membranes with selectivities ranging from 11.0 to 14.0. These membranes were found to be quite stable over time periods of several days with high-purity, dry feeds [41]. Three years later Hiroyuki Suda and Kenji Haraya prepared and studied carbon molecular sieve membranes by pyrolysis of Kapton polyimide films under several conditions. They report that with decreasing the pore sizes upon pyrolyzation under vacuum, the gas permeability decreased, whereas the permselectivity increased. They also found that the change in the heating rate affects the permeation properties to a lesser extent; however, the pyrolysis atmosphere (vacuum or inert purge pyrolysis) did not significantly influence the properties within the experimental conditions studied. The highest permselectivities achieved were H<sub>2</sub>/N<sub>2</sub>: 4700, He/N<sub>2</sub>: 2800, CO<sub>2</sub>/N<sub>2</sub>: 122, and O<sub>2</sub>/N<sub>2</sub>: 36, respectively, at 308 K. The gas permeance values were shown to be in the order H<sub>2</sub> > He > CO<sub>2</sub> > O<sub>2</sub> > N<sub>2</sub> for almost all studied membranes, and not exactly in accordance with the order of kinetic gas diameters [42].

In 2003, De Q. Vu and coworkers developed mixed matrix membranes by adding carbon molecular sieves (CMS) into two different polymer matrices. The CMS membrane films were formed by the carbonization of Matrimid® polyimide precursor to a final temperature of 1073 K. These CMS membrane films have an intrinsic CO<sub>2</sub>/CH<sub>4</sub> selectivity of 200 with a CO<sub>2</sub> permeability of 44 Barrers and an O<sub>2</sub>/N<sub>2</sub> selectivity of 13.3 with an O<sub>2</sub> permeability of 24 Barrers at 308 K. They also concluded that the effective permeabilities of the fast-gas penetrants (O<sub>2</sub> and CO<sub>2</sub>) through the mixed matrix membranes were also significantly enhanced compared to the intrinsic permeabilities of the Ultem® and Matrimid® polymer matrices. This improved combination of selectivity and permeability confirm that mixed matrix membrane behavior is feasible with the addition of CMS particles [43]. Centeno and coworkers in their work entitled “Effects of phenolic resin pyrolysis conditions on carbon membrane performance for gas separation” showed that the gas separation performance of phenolic resin-based carbon membranes can be adjusted by controlling the pyrolysis processing variables [44]. In 2008 Anderson et al. studied the effect of pyrolysis temperature and operating temperature on the performance of nanoporous carbon membranes [45] and many other researchers, including our group [17,39,46], have published hundreds of interesting works relevant to this field.

In this work the effect of the pyrolysis conditions on the gas permeation properties of carbon molecular sieve (CMS) hollow

fiber membranes was investigated. Specifically, BTDA-TDI/MDI (P84) co-polyimide [47] hollow fiber membranes were carbonized at 1173 K and the isothermal time at the highest temperature was 5, 30 and 60 min at each case. For all experiments the heating rate was kept constant at 5 K/min and the inert pyrolysis atmosphere was pure Argon gas.

## 2. Experimental

### 2.1. Preparation of carbon molecular sieve membranes

We have selected BTDA-TDI/MDI (P84) co-polyimide as a precursor material for the preparation of the carbon membranes due to the fact that it presents good thermal properties, high resistance in harsh chemical environments as well as excellent mechanical strength. This fact has been thoroughly discussed in the literature [17,26,39,46,48,49]. In the current work P84 was spun by using dry-wet spinning process to form hollow fiber membrane. Specifically, BTDA-TDI/MDI, (P84), co-polyimide hollow fibers were developed by the dry/wet phase inversion process via spinodal decomposition [50–52]. The involved spinning set up is already described in a previous work [17] as well as the used oven was also described previously [23,39]. Before the pyrolysis procedure the precursor membranes were stabilized for 1 h at 373 K to alter the chain packing or chain segmental mobility of the polymer and, therefore, the structural organization of membrane [53,54].

In all cases, 150 ml/min of Argon was sweeping the inner side of the furnace tube while a heating rate of 5 K/min was applied.

Table 1 shows that, the maximum pyrolysis temperature was 1173 K while the stabilization time at this temperature was 5, 30 and 60 min.

### 2.2. Gas permeance measurements

Gas permeances were measured by two techniques, the first one is the “variable pressure method” and the second is the “flow method” using gas chromatography. In the first technique the permeate stream is accumulated in a standard vessel and the permeance is calculated by the pressure transition during the measurement time by continuously monitoring the pressure increase in the low-pressure side of the membrane rig by means of an accurate differential pressure transducer. In all cases, the feed pressure of each measured gas has been kept constant. Details for this kind of apparatus can be found in our previous works [46,55].

Pure gas permeance values, were determined using the following formula [46,56]:

$$\bar{P} = \frac{V \cdot 273.15 \cdot (p_t - p_0)}{76 \cdot A \cdot T \cdot (1/2) \cdot (P_t - P_0) \cdot t} \cdot 10^6$$

where the ideal gas law is assumed to be valid. Here,  $t$  (s) is the time,  $p_t$  (bar) is the pressure at the permeate side at time  $t$ ,  $p_0$  the permeate pressure at time  $t=0$ ,  $P$  (bar) the feed pressure,  $T$  (K) the temperature,  $V$  (cm<sup>3</sup>) the calibrated permeate volume and  $A$

**Table 1**

Pyrolysis conditions of three produced carbon molecular sieve hollow fiber membranes from the same P84 co-polyimide precursor.

	Carbon hollow fiber membrane		
	CMS-900/5	CMS-900/30	CMS-900/60
Pyrolysis atmosphere	Argon	Argon	Argon
Heating rate	5 K/min	5 K/min	5 K/min
Maximum pyrolysis temperature	1173 K	1173 K	1173 K
Isotherm time at maximum temp.	5 min	30 min	60 min
Cooling rate	10 K/min	10 K/min	10 K/min

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