LATEST DEVELOPMENT OF CARBON HOLLOW FIBER MEMBRANES FOR GAS SEPARATION

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ABSTRACT

Inorganic membrane is one type of synthetic membranes. It has been developed before 1945. At early stage, the application of inorganic membranes was mainly concentrated on military purpose and not commercially used by the industry. However, nowadays inorganic membranes especially carbon membrane has emerged as another alternative membrane in the separation technology. Generally, inorganic membranes can be divided into two different categories: porous inorganic membranes and dense inorganic membranes. Carbon molecular sieve membrane is one type of porous inorganic membranes. The concept of carbon membrane for gas separation has been found in early 1970. However, the boost of interest to develop carbon molecular sieve membrane only appeared after Koresh and Soffer successful achieved apparently crack-free molecular sieving carbon hollow fiber membranes. Until today, researchers from all over the world have prepared carbon molecular sieve membranes by using various polymeric materials. Pyrolysis method is usually used to produce carbon membranes derived from organic polymers. Permeation properties of carbon membranes have been improved greatly in these 20 years due to much effort put in this field. It is found that the carbon membrane has a lot of unique characteristic and advantages compared with polymeric membranes. Due to better selectivity, thermal and chemical stability, more attention will be paid to carbon membranes in new millennium especially carbon hollow fiber membranes. This is because hollow fiber configuration has been recognized to be more suitable and practical to be used in the industry. Hence, the purpose of this paper is to give an overview regarding the development of carbon hollow fiber membranes in last 30 years in order to encourage more researchers involve in the development of carbon hollow fiber membranes for gas separation.

Keywords: Inorganic membrane, porous, hollow fiber, carbon molecular sieve

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1. Introduction

Since 1945 and even before, the porous inorganic membranes have been developed long before the development of today's synthetic organic membranes. First porous inorganic membranes were developed for separation of uranium isotopes, which were mainly used for military purposes [1]. The potential of inorganic membranes were not widely recognized until high quality porous ceramic membranes were produced for industrial usage on a large scale [2]. Nowadays, inorganic membranes are used primarily for civilian energy-related applications. Since then, they have become important tools for the separation of dairy products and industry separation processes [1].

Hsieh has divided the inorganic membranes into two major categories: porous inorganic membranes and dense (nonporous) inorganic membranes. Porous inorganic membranes with pores more than 0.3 nm usually work as sieves for large molecules and particles. Glass, metal, alumina, zirconia, zeolite and carbon membranes are the porous inorganic membranes commercially used. On the other hand,

dense membranes made of palladium and its alloys, silver, nickel and stabilized zirconia have been used mostly for separating gaseous components. Dense membranes primarily applied in highly selective separation of hydrogen and oxygen; transport occurs via charged particles. However, due to their low permeability compared to porous inorganic membranes, the dense membranes are very limiting for industrial application [1, 2, 3].

Although inorganic membranes are more expensive than organic polymeric membranes, their unique characteristics: temperature and wear resistant enable them to compete with polymeric membranes. In addition, the porous inorganic membranes have a well-defined stable pore structure and are chemically inert. These advantageous characteristics of inorganic membranes encouraged many researchers in the early 1980s to investigate the gas separation properties of these membranes especially porous inorganic membranes [1].

At present, interest in the development of porous inorganic membranes based on materials providing better selectivity, thermal selectivity and chemical stability than those already existing (i.e. polymeric membranes) has been grown. The attention has been focussed on materials that exhibit molecular sieve properties such as silica, zeolites and carbon, which are suitable for gas separation as shown in the Figure 1 [4]. Silica-based inorganic membranes can selectively separate hydrogen from other gases. However, permselectivity between similar-sized molecules such as oxygen and nitrogen is not sufficient [5]. Zeolites can separate isomers, but it is difficult to obtain a large, crack-free zeolite membrane. Hence, it is more feasible to form carbon molecular sieve membrane [5, 6]. Therefore, this paper will give an overview regarding development of carbon hollow fiber membranes in past 30 years. Future direction and the trend of carbon membranes development in the new millennium will also included.

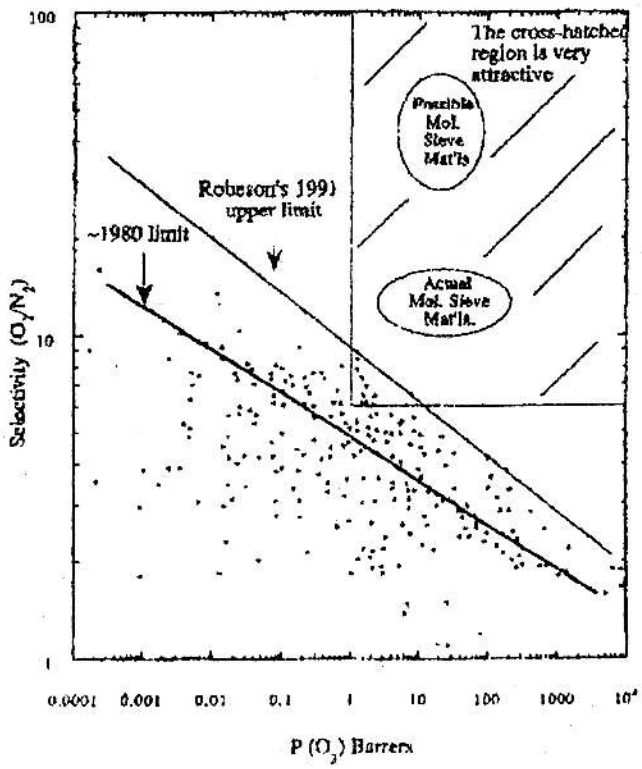

FIGURE 1: Comparison Between Properties of Polymeric Membranes and Molecular Sieve Membranes with the Upper Limit of Performance [7].

2. Transport Mechanism of Carbon Membranes

Mass transfer of gas through a porous plug can involve several processes, depending on the nature of the pore structure and the solid [8]. In general, there are 4 different mechanisms for separation of a gas

mixture through porous membrane: Knudsen diffusion, partial condensation/capillary condensation, surface diffusion/selective adsorption and molecular sieving [2, 9]. The transport mechanism owned by the carbon membrane is molecular sieving mechanism as shown in Figure 2.

The carbon membranes contain constrictions in the carbon matrix, which approach the molecular dimensions of the diffusing gas molecules [10]. At these constrictions the interaction energy between the molecule and the carbon is comprised of both dispersive and repulsive interactions. When the opening becomes sufficiently small relative to the size of the diffusing molecule, the repulsive forces dominate and the molecule requires activation energy to pass through the constrictions. In this manner, molecules with only slight differences in size can be effectively separated through molecular sieving in the region of activated diffusion [11]. According to this mechanism, the separation is caused by passage of smaller molecules of a gas mixture through the pores while the larger molecules are obstructed. It exhibits high selectivity and permeability for the smaller component of a gas mixture [9]. Carbon matrix itself is impervious suggests that permeation through carbon membranes can be attributed entirely to the pore system. Therefore, the mechanism of gas permeation and uptake through porous solids is closely related to the internal surface area and dimensions of the pores and to the surface properties of the solid, rather than to its bulk properties of the solid [12].

However, carbon membrane requires a very fine control of the pore sizes (diameter < 4Å) and requires operation at an elevated temperature in order to provide practically acceptable flux for the smaller molecules due to this membrane has thickness of several microns [9].

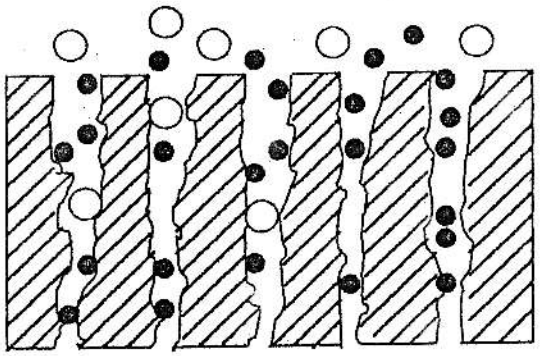

FIGURE 2: Molecular Sieving Transport Mechanism [13]

3. Carbon molecular sieve membranes

The concept of carbon molecular sieve membrane or film for gas separation can be found in the early 1970. Barrer et al. prepared carbon membranes by compressed non-porous graphited carbon into a plug [14]. Bird and Trimm used polyfurfuryl alcohol (PFA) to prepare unsupported and supported carbon molecular sieve membranes. They met shrinkage problem during carbonization. That problem would lead to cracking and deformation of the membrane. Hence, they unable to obtain a continuous membrane [8].

Carbon molecular sieves produced from the pyrolysis of polymeric materials have proved to be very effective for gas separation by Koresh and Soffer [15, 16, 17, 18]. Molecular sieve carbon can be easily obtained by pyrolysis of many thermosetting polymers such as poly(vinylidene chloride) (PVDC), poly(furfuryl alcohol), cellulose, cellulose triacetate, saran copolymer, polyacrylonitrile, phenol formaldehyde and various coals such as coconut shell [15]. They reported that the pore dimensions of carbon were depending on morphology of the organic precursor and the chemistry of pyrolysis [19].

The interest in developing carbon membranes only grown after Koresh and Soffer [12, 19, 20] had successfully prepared apparently crack-free molecular sieving hollow fiber membranes by carbonizing cellulose hollow fiber. They have shown the dependence of permeabilities and selectivities on temperature, pressure and extent of pore for both adsorbing and non-adsorbing permeates [19, 20]. However, those membranes would be lack of mechanical strength for practical application.

Carbon membranes usually can be divided into two categories: unsupported and supported carbon membranes [4]. Unsupported membranes have 3 different configurations: flat (film), hollow fiber and capillary while supported membranes consisted of two configurations: flat and tube.

Literature review showed that most of the carbon membranes produced during 1980-an until early 1990an were flat disk or flat sheet membranes. During the middle of 1990-an, carbon membranes supported on tube have been made followed with carbon capillary membranes and carbon hollow fiber membranes. Flat sheet carbon membranes are more suitable for laboratory or research applications while carbon membranes supported on tube, carbon capillary membranes and carbon hollow fiber membranes are more practical and suitable to apply in industry. Therefore, this paper will concentrate on the discussion regarding the development of carbon hollow fiber membranes.

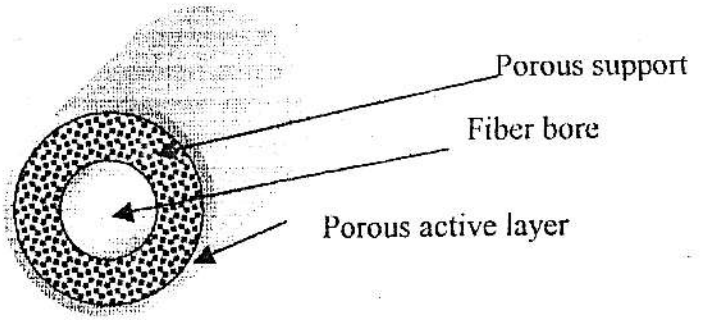

FIGURE 3: Carbon Hollow Fiber Membrane.

4. Carbon Hollow Fiber Membranes

Linkov et al. [21] reported that the carbonization of highly asymmetrical PAN precursors resulted in the formation of a range of flexible hollow fiber carbon membranes with high porosity and good mechanical properties. Morphology of carbon membrane and the possibility of altering of the pore structure were studied. They proposed that precursor preparation (solution formulation and fabrication procedure) and stabilization as well as carbonization conditions have possibility to alter the pore sizes of carbon membranes.

Linkov et al. [22] also have coated carbon hollow fiber membranes by using vapour-deposition polymerization method. Then, they produced composite carbon-polyimide membranes by heating in a nitrogen atmosphere. The composite membranes have resistance against high pressures and high flexibility. The membranes had low wall and active skin thickness with good mechanical properties.

Jones and Koros chose polyimide derived from a reaction of 2,4,6-trimethyl-1,3-phenylene diamine,5,5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidenel]-1,3-isobenzofurandione and 3,3',4,4'-biphenyl tetra carboxylic acid dianhydride to prepare carbon molecular sieve asymmetric hollow fiber membranes [11]. Although those membranes were developed and optimized for air separation applications, the membranes were able to separate other gas mixtures for example CO_2/N_2, CO_2/CH_4 and H_2/CH_4 effectively. The selectivities of the carbon membranes were much higher than those seen with conventional polymeric materials with acceptable productivity. Furthermore, those membranes were found to be quite stable over time period of several days with high purity and dry feeds.

On the other hands, Jones and Koros have discovered a few problems or weakness of carbon membranes during their studies [10, 23]. It was known that carbons generally have nonpolar surfaces and as a result are organophilic. Therefore, ultramicroporous carbon membranes would be very vulnerable to adverse effects from exposure to organic contaminants due to its adsorption characteristics of organics. As a result, a unique regeneration technique has been developed by Jones and Koros [23] to remove organic contaminants. They found that pure propylene at unit or near-unit activity was suitable for the regeneration process. The propylene most likely acted as a cleaning agent, removing other sorbed compounds from the carbon surface and recovered the membrane performance.

Jones and Koros [10] also found that the micropores of carbon membranes were gradually plugged with water at room temperature and resulting in the decrease of the non-polar gases permeabilities and its selectivities. When the surface of carbon membrane is partially covered with oxygen-containing functional groups, bring the membrane having a hydrophilic character [24]. The studies showed that the capacity of other species was diminished as the quantity of sorbed water in microporous carbon adsorbents increased [10]. The problem was overcome by coating the membrane with a highly hydrophobic film, which did not prohibitively reduce the flux of other permeating species. Therefore, the resulting carbon composite membranes demonstrated a greater resistance to the adverse effects from water vapor without sacrificing its separation properties [25].

Besides that, Geiszler and Koros [26] have studied the effect of polyimide pyrolysis conditions on carbon molecular sieve membranes performance. They compared the differences between carbon membranes properties prepared by vacuum pyrolysis and inert purge pyrolysis. In addition, they also studied other pyrolysis variables such as the processing temperature, purge gas flowrate and residual oxygen concentration in the purge gas. They observed that pyrolysis atmospheres and flow rates of purge gas strongly influenced H_2/N_2 and O_2/N_2 selectivities of carbon molecular sieve membranes.

Kusuki et al. [27] have prepared the asymmetric carbon membranes by carbonization of asymmetric polyimide hollow fiber membranes. The effects of different experimental conditions on the membrane performance have been studied. The carbon membranes they obtained showed high permselectivities as reported by other researchers.

Tanihara et al. [28] also made the asymmetric carbon membranes by carbonization of asymmetric polyimide hollow fiber membranes. In their study, they found that the permeation properties of carbon membrane were hardly affected by feed pressure and exposure of toluene vapor. In addition, there was only little change in the permeation properties of the carbon membrane with the passage of time.

Ogawa and Nakano [29] have put effort to investigate the effect of gelation conditions on the properties of the carbonized membrane. The carbonized hollow fiber membrane was formed by gelation of polyamic acid (PAA) solution in a coagulant by phase inversion method, imidization and carbonization. The microstructure of the carbonized membrane was evaluated by the micropore volumes, which depended on gelation temperature and pH of coagulant. Hence, they reported that the gelation process was important factor to control microstructure, permeance and permselectivity of the carbonized membrane However, they observed that the gelation time was not a predominant factor to control the micropore volume, the permeances and CO_2/CH_4 permselectivity.

They realized that the high permeance of CO_2 and the high CO_2/CH_4 permselectivity were obtained under the specific conditions of gelation: time 6h, temperature 275K and pH 9.4. They concluded that the transport of CO_2 was mainly governed by the adsorption effect while transport of CH_4 was restricted by the molecular sieving effect. As a result, yielding high CO_2/CH_4 permselectivity [29].

Table 1 has summarized the researchers who are involved in the development of carbon hollow fiber membranes. It is clear to see that more researchers are interest to study hollow fiber membranes in last 10 years. It is due to hollow fiber membranes have a lot of advantages compare with flat sheet membranes or other types of membrane configurations. Two main advantages of hollow fiber are self supporting and exhibit higher productivity per unit volume [30].

TABLE 1: Carbon Hollow Fiber Membranes Produced by Previous Researchers

Researcher(s)	Period/Year	Reference(s)
Koresh & Soffer	1980-1987	12, 15, 19, 20
Linkov et al.	1994	21, 22
Jones & Koros	1994-1996	10, 11, 23, 24, 25
Kusuki et al.	1997	27
Geiszler & Koros	1999	26
Tanihara et al.	1999	28
Ogawa &Nakano	1999	29

5. Application of Carbon Membranes

The most important large application of carbon molecular sieve is in the production of low cost and high purity nitrogen from air. Other applications are including separation of hydrogen from gasification gas and purification of methane [31].

In addition, it is also used to recover a valuable chemical (H_2) from a waste gas without further compression of the feed gas while rejecting a substantial portion of the hydrocarbons [9].

6. Current Research and Future Direction

Increasing interest in gas separation by organic membranes has lead to exploitation of inorganic membranes for high temperature or corrosive gas separation applications [2]. Nowadays, inorganic membrane producers are generally in the start-up and technology push stage. Meanwhile, the end-user industry has exhibited a "wait-and-see" attitude when it comes to adopting advanced inorganic membrane applications. Industries currently interest to know the performance of inorganic membranes in separation process and their stability in aggressive environment [1].

In general, gas separation inorganic membranes can be categorized into 3 types consisted of microporous, amorphous membranes; microporous, crystalline membranes and dense, high temperature membranes. Keizer and Verweij proposed that a lot of attention would be focused on realizing complex, well-defined porous architectures. They believed all these 3 types of membranes would be combined to new separation properties with improved long-term stability in these few years. In the near future a gradual shift will take place from the exploration of new membrane concepts toward better control of membrane preparation and understanding of performance, long-term stability and process integration in the applications [1].

Currently, porous ceramic membranes dominate commercialized inorganic membranes. The most prevalent membrane materials are metallic oxides and more precisely alumina and zirconia, but other materials, such as titania, carbon or glass are available. There are only a few manufacturers involved in the production of carbon membranes [3].

Hence, carbon membranes still need a lot of improvement to become dominant commercialized inorganic membranes in the future. Investigation on material selection of more suitable precursor to produce carbon membranes is necessary. Finding and producing a more economical material than polyimide and polymeric material recently used is a necessary trend in carbon membrane production. Carbon membranes have a great potential to replace other inorganic membranes in the market because they are able to separate efficiently gas mixtures, which have similar size of gas molecules. Hence, Membrane Research Unit (MRU) at University Technology Malaysia has now started to study and develop asymmetric carbon hollow fiber membrane for gas separation application.

7. Conclusions

As we can see from the previous researches, the carbon hollow fiber membrane has emerged as another alternative membrane to be used in the separation process especially for gas separation. The advantages possessed by the carbon hollow fiber membranes compared with other configurations of carbon membranes make it become more attractive among the carbon membranes researchers. Its unique characteristics and advantages make it comparative with polymeric membrane even with other porous inorganic membrane. It has a bright future. However, a lot of research and development efforts shall put in order to commercialize the carbon membrane widely in the international market.

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