Formation of Carbon Membrane from Polyacrylonitrile (PAN) Hollow Fiber Membrane for Gas Separation

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Introduction

There is a growing interest in the development of gas separation membranes that can give higher performance of membrane, with better chemical and mechanical properties in both corrosive and high temperature operation. One of the most popular materials is carbon-based material (Saufi and Ismail, 2004).

Carbon membrane can be produced by pyrolysis of suitable polymeric membrane precursor in a controlled condition and atmosphere. Lately, numerous precursors have been used to form carbon membrane such as polyimides and derivatives, polyacrylonitrile (PAN), phenolic resin, poly (vinylidene chloride), poly (furfuryl alcohol), cellulose, phenol formaldehyde, polyetherimide and polypyrrolone (Saufi and Ismail, 2002). Although polyimides is mostly used as a precursor and give good performance of membrane, their limited availability and high price become an obstruction factor in the development of polyimides-based carbon membrane in Malaysia. Therefore, in order to reduce the cost and time during fabrication of carbon membrane, we have extensive study the formation of carbon membrane from PAN precursor (Saufi and Ismail, 2002; 2004; David and Ismail, 2003). The advantages of PAN as a precursor of carbon membrane can be found in this paper (Saufi and Ismail, 2002).

In general, the fabrication of carbon membranes involves six important steps, as shown in Figure. 1. At the same time, there are several factors that need to be considered in order to ensure the success of each step. Among these steps, the pyrolysis process is the most important step and can be regarded as the heart of the carbon membrane production process.
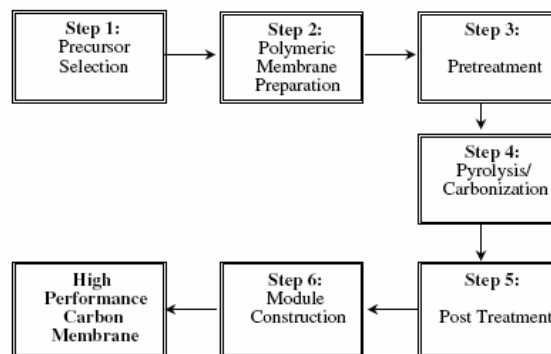

FIGURE 1 Carbon membrane fabrication process (Saufi and Ismail, 2004)

In the present paper, we have studied two important parameters that are dope extrusion rate (DER) during the polymeric membrane preparation and pyrolysis temperature during the pyrolysis process. The PAN carbon membrane was fabricated in the form of hollow fiber membrane and was applied for pure O_2/N_2 gas separation. The following section will explain in detail about the preparation of the membrane.

Methodology

Dry/wet spinning of PAN hollow fiber membranes

The polymer solution consisting of 15 wt% PAN (Aldrich18131-5) is dissolved in 85wt% dimethylformamide (DMF) was used as a spinning dope. The dry/wet spinning technique has been used with the spinneret located about 9 cm from the water bath. During the spinning process, the DER was varied from 1.0 to 3.0 in order to induce different level of shear rate (Ismail et al., 1999) during the formation of PAN hollow fiber polymeric membranes. The fully formed hollow fiber membrane has a
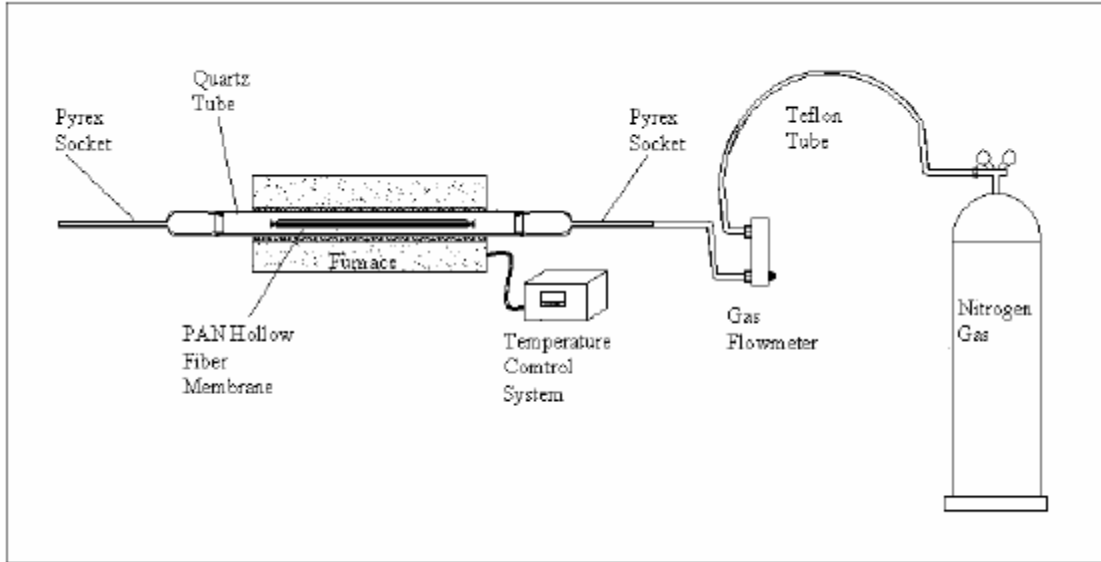
FIGURE 2 Nitrogen inert gas pyrolysis systems for producing PAN carbon hollow fiber membrane (Saufi and Ismail, 2004; 2002).

dimension of 600μm and 300μm of outside and inside diameter respectively. Before undergoes drying process, the membrane was subjected to the solvent exchange process in water, methanol and hexane for 2 days in each bath respectively.

Nitrogen inert gas pyrolysis system

Nitrogen inert gas pyrolysis system was set up as shown in Figure 2. Around 25-30 pieces of PAN fiber were pyrolyzed for each run. Before starting the pyrolysis, the PAN membrane was subjected to the thermostabilization in air at 250°C for 30 minute at heating rate of 5°C/min. After thermostabilization, the inert gas needed to be purged into the pyrolysis system to remove the unwanted air or oxygen. This was to prevent the oxidation from occurring during high temperature pyrolysis process. Then, the precursor was heated to a required pyrolysis temperature in the range of 500-800°C and maintained at that temperature for 30 min by setting up the temperature control systems. The heating rate was set at 3°C/min and nitrogen gas flow rate was maintained at 200 cm^3/min. The resulting carbon membrane was cooled down to ambient temperature in an inert gas atmosphere (Saufi and Ismail, 2004).

Permeation test

Before the permeation test was run, the carbon hollow fiber membrane must be potted in a bundle consisting about 5 to 10 fibers. One end of the fiber bundle was sealed into a stainless steel tube of 5/8 inch outer diameter, while the dead end part was potted in an aluminium cap. Loctite E-30CL epoxy adhesive was used as a potting resin.

The entire single gas permeation system used during this study is illustrated in Figure 3. Pure O_2 and N_2 were introduced into the system at feed pressure of 5 bar at ambient temperature. The permeate side of membrane was maintained at atmospheric pressure. Simple soap film flow meter was used to obtain the permeation properties of the gas owing to its suitability for the measurement of small and wide range flow rates (Kusuki et al., 1997).

The pressure-normalized flux and selectivity of the carbon membrane was calculated from the collected data by using equation (1) and equation (2) respectively

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{\Delta p.A} \tag{1}$$

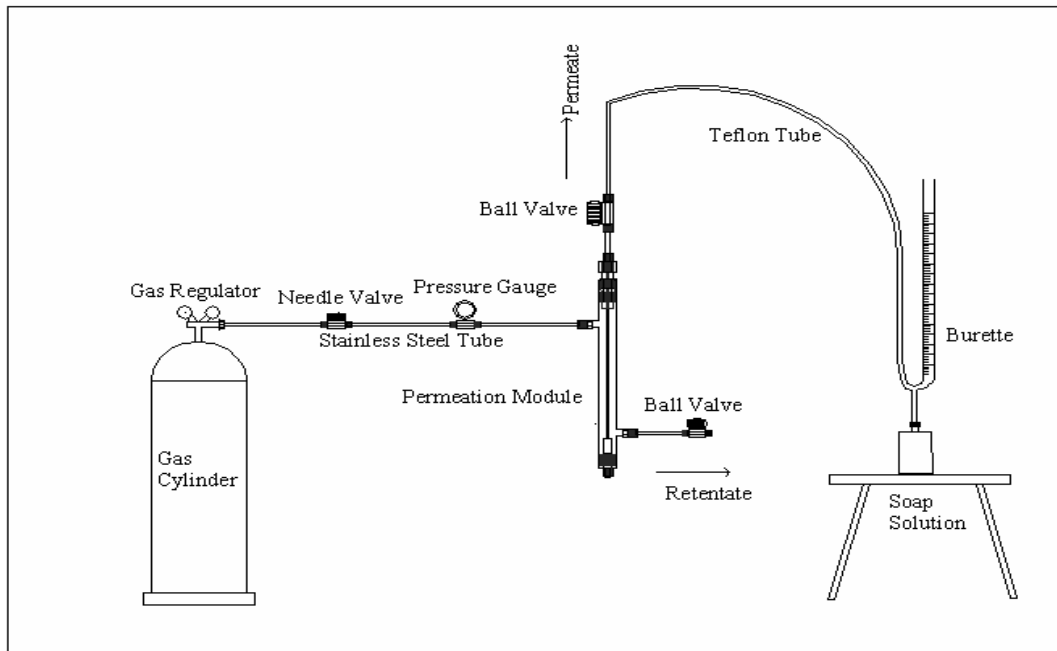$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B} \tag{2}$$

FIGURE 3: Pure O_2 and N_2 gas permeation testing system.

Where; $(P/l)_i$ is pressure-normalized fluxes, Q_i is volumetric flow rate of gas, Δp is transmembrane pressure drop, A is surface area of membrane and $\alpha_{A/B}$ is ideal separation factor or selectivity. The permeability unit that was usually applied in membrane research is gas permeation unit (GPU) and Barrer. In this study, GPU (1 GPU = 1×10^{-6} cm^3(STP)/cm^2.s.cmHg) was used due to the facts that the exact value of membrane skin thickness is difficult to attain and determine since the membrane is in asymmetric form.

Results and Discussion

Effects of dope extrusion rate on O_2/N_2 gas separation of PAN polymeric hollow fiber membrane

Many study had prove that shear rate can alter the separation performance of polymeric membranes even sometimes surpass the intrinsic selectivity of the polymer itself (Ismail *et al*., 1999; Sharpe *et al*., 1999). When PAN solution was extruded from the spinneret, they were subjected to various stresses which may influence molecular orientation of the polymer, fiber formation mechanism, as well as the separation performance of the membrane

(Chung *et al*., 2000a). However, previous study had showed that a critical shear rate was existed when a polymer solution being subjected to the different level of shear (Sharpe *et al*., 1999; Chung *et al*., 2000b; Ismail and Lai, 2003).

Table 1 summarizes the gas permeation data of PAN hollow fiber membrane at different level of shear for the O_2 and N_2 gases and Figure 4 shows the pressure-normalized flux and selectivity of the PAN membrane plotted at different shear rates. From Figure 4, it can be seen that critical shear rate existed which the optimum selectivity was achieved at a value of about 0.95. Prior to the critical shear, both pressure-normalized fluxes and selectivity were increased with increasing shear rate. However, over the critical shear rate the selectivity dropped sharply whereas the pressure normalized flux was increased.

TABLE 1 Pressure-normalized flux and selectivity of pure oxygen and nitrogen of PAN hollow fiber membranes at different DER

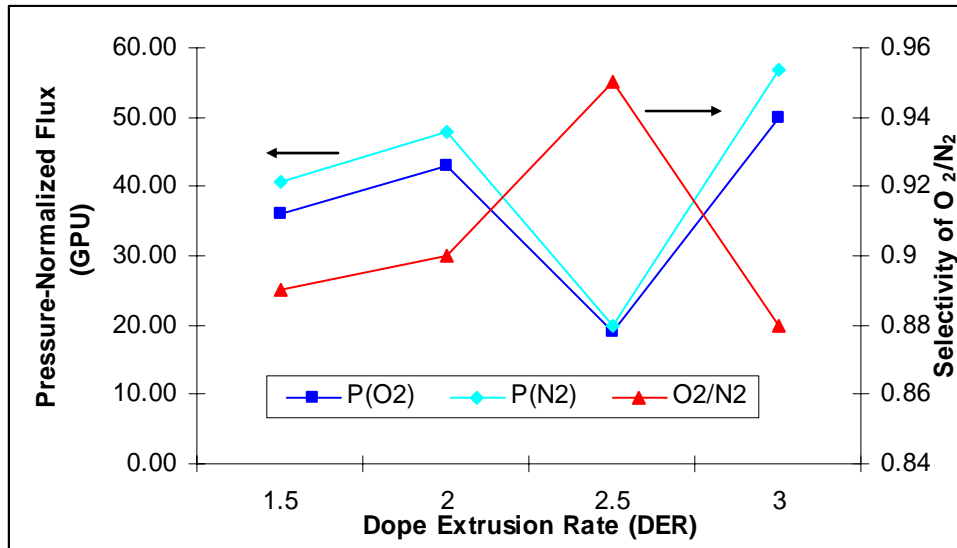| DER	P (O_2) GPU	P (N_2) GPU	α (O_2/N_2)
1.5	36.16	40.56	0.89
2.0	43.09	47.78	0.90
2.5	19.03	19.98	0.95
3.0	49.96	56.86	0.88

FIGURE 4 Selectivity of O_2/N_2 and pressure-normalized flux of oxygen and nitrogen for PAN hollow fiber membrane spun at different DER.

At the early stage, selectivity is increased prior to the critical shear probably due to the shear induced molecular orientation in the PAN polymer molecules. This phenomenon leads to a tighter structure in skin layer which result in an improve membrane selectivities (Ismail et al., 1997; Chung et al.; 2000a; Ismail and Lai, 2003). Pressure-normalized flux was also found to be increasing with the increase of shear rate, which was consistent with an increase of surface pore area and free volume as been reported by Shilton et al. (1994) and Ismail and Lai (2003).

Pressure-normalized flux was found to be decrease with the increasing of shear rate from DER 2.0 to DER 2.5. This was due to shear-induced chain packing and orientation of the polymer molecules which produce thicker skin layer and lower free volume structure (Wang and Chung, 2001; Chung et al., 1998). Therefore, the O_2 and N_2 gases transport resistance increased by this tighter structure and consequently the pressure-normalized flux for both gases will reduce (Chung et al., 1998).

Beyond the critical shear rate at DER 2.5, the selectivity of PAN hollow fiber membrane was reduced drastically, while the pressure-normalized flux increased. Since the PAN solution was shear-thinning, as shear rate reached beyond the critical point, a severe decrease in solution viscosity occurred presumably due to chain entanglement losses in solution. In this case, membrane might undergo an early demixing and precipitation to result in a porous and highly oriented skin layer (Chung et al., 2000b). Furthermore, spinning of PAN membrane at an extremely high shear (over the critical shear rate) pulled molecular chains or phase-separated domains apart and began to create slight imperfections or defects in skin layer (Sharpe et al., 1999).

Effects of pyrolysis temperature on O_2/N_2 gas separation of PAN carbon hollow fiber membrane

Table 2 summarizes the gas permeation data of PAN carbon hollow fiber membrane pyrolysis at different temperature for the O_2 and N_2 gases. Figure 5 shows the pressure-normalized flux and selectivity of the PAN carbon hollow fiber membrane plotted at different pyrolysis temperature for O_2/N_2 gas separation.

TABLE 2 Pressure-normalized flux and selectivity of pure oxygen and nitrogen of PAN carbon hollow fiber membranes at different pyrolysis temperature

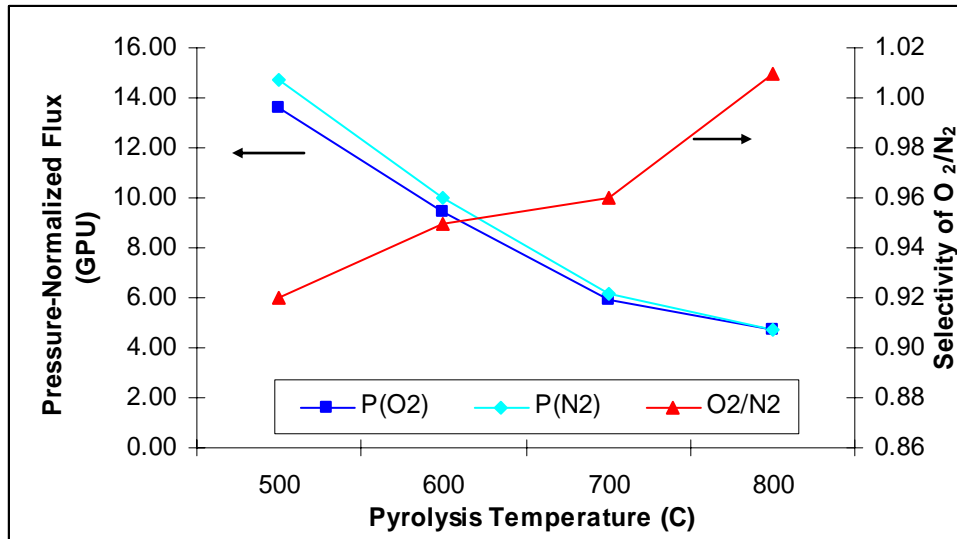| Temperature (°C)	P (O_2) GPU	P (N_2) GPU	α (O_2/N_2)
500	13.62	14.74	0.92
600	9.47	10.00	0.95
700	5.92	6.20	0.96
800	4.74	4.70	1.01

FIGURE 5 Selectivity of O_2/N_2 and pressure-normalized flux of oxygen and nitrogen for PAN carbon hollow fiber membrane pyrolyzed at different pyrolysis temperature.

As shown in Figure 5, both O_2 and N_2 pressure-normalized flux decreased with increasing the pyrolysis temperature. The extent of this reduction is more noticeable between pyrolysis temperatures of 500°C to 700°C. The reduction in pressure-normalized flux of gases depicted that the pore structure in PAN carbon membrane become smaller with increasing pyrolysis temperature. According to Suda and Haraya (1995), high temperature pyrolysis would cause a higher crystallinity, density and narrower interplanar spacing of graphite layers of the carbon, which produces a carbon membrane with small pore size structure. Furthermore, the asymmetric structure of the membrane becomes dense due the physical shrinking of the membrane with a decomposition and evolution of the byproducts as the pyrolysis temperature increases. All of these factors were contributed to a reduction of pressure-normalized flux in PAN carbon hollow fiber membrane as the pyrolysis temperature increases.

At early stage of pyrolysis process, it was believed that the selectivity of the membranes decreased due to the pore formation on the surface of the membrane that is induced by the evolution of the volatilities in the polymer (David, 2001). However, based on the result shows in Figure 5, pyrolysis temperature of 500°C already contributed to the increment of selectivity in PAN carbon hollow fiber membrane. This means that the pore formation in PAN carbon hollow fiber membrane already started below this temperature, thus it is also feasible to pyrolysis the PAN membrane below 500°C.

Obviously from Figure 5, the increasing of pyrolysis temperature will produce more selective carbon hollow fiber membrane. Highest selectivity for O_2/N_2 by was achieved at 800°C which is around 1, but we believe that further increment can be achieved by further increasing pyrolysis temperature. This is because as the pyrolysis temperature is increases, gradual destruction of crosslinks in polymeric membrane occurs which leads to clustering of the aromatic units and subsequent rearrangement of stacking graphite planes. The alignment of graphitic structures leads to micropores closing on increasingly severe thermal treatment conditions (Centeno et al., 2004). Moreover, at high temperature, it was proposed that a thin layer of carbon could be deposited inside the pores without sealing them. As a result, average pore size was being modified or reduced without complete pore blocking, thus the increment of membrane selectivity and reduction of permeability could be detected (Geiszler and Koros, 1996).

Based on the permeation results obtained, all the selectivity value achieved by PAN carbon

hollow fiber membrane is just slightly above the Knudsen selectivity (i.e. $\alpha\ O_2/N_2 = 0.94$). One of the probable reasons for the low selectivity of the PAN carbon membrane was due to the lower selectivity of the initial PAN precursor. Although the pyrolysis process had improved the selectivity of the membrane as reported with other precursor, but this increment was not pronounced in the case of the PAN based carbon hollow fiber membrane. One way that can be considered in the future is to fully optimize the preparation condition of the PAN polymeric precursor to give better precursor properties. This area of the research especially with PAN hollow fiber membrane used for gas separation is still not fully explored yet.

Another possibility that contributed to lower selectivity in PAN carbon membrane is the presence of surface defects in the membrane surface which diminish the ability of membrane to perform molecular sieving characteristic. Thus, further study on the mechanism of pore formation in PAN polymer degradation during pyrolysis is important in order to tailor made the pore structure in the PAN carbon membrane. Precise control of pore formation in PAN membrane may result in significant improvement in PAN carbon hollow fiber membrane for gas separation.

Conclusion

The highest selectivity of PAN carbon membrane for O_2/N_2 gas separation achieved is about 1. Although the separation performance is not as competitive compared to the available precursor, we had discussed in details the science behind developing carbon hollow fiber membrane from PAN. Perhaps this scientific background can be further explored in order to develop a more competitive carbon hollow fiber membrane from PAN. In addition, we believed that the manipulation of pyrolysis process parameter can give more pronounce effect in order to tailor made the performance of PAN carbon membranes.

Acknowledgement

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