

# **DEVELOPMENT OF GAS SEPARATION SYSTEM BY MEMBRANES- PRELIMINARY RESULTS OF MEMBRANES CHARACTERIZATION**

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## **ABSTRACTS**

The huge natural gas found in Malaysia has necessitated research and development in new technologies for gas processing. Membranes technology is not only the latest and most advanced system but also requires less cost of maintenance. This paper presents the preliminary results of membrane characterization for CO<sub>2</sub> separation from natural gas. It is a part of the overall project to develop CO<sub>2</sub> gas separation system using membrane from natural gas funded by IRPA.

Polymeric membrane suitable for gas separation was developed from polymer solution casted on a glass plate. Phase inversion technique was then used which produced asymmetric membranes with a very thin skin on top of porous substrate.

The asymmetric structure is an essential properties for high flux and high selectivity required for gas separation. The membranes were then characterized in term of their structure using a Scanning Electron Microscope (SEM). A gas permeation cell was then used to measure the pure gas permeation rates through the membranes.

Preliminary results of membranes characterization show that asymmetric structure was successfully produced with thin layer of skin deposited on the porous substrate. However the skin thickness needs to be reduced before a good membrane performance can be obtained as evidenced by the flux measurement data obtained.

Work is currently focused on the parameters such as temperature and annealing process which influenced the formation of ultra thin skin on top of porous substrate.

## **ABSTRAK**

Simpanan gas asli yang banyak dijumpai di Malaysia memerlukan penyelidikan dan perkembangan dalam teknologi baru untuk pemisahan gas. Teknologi membran bukan sahaja sistem terkini dan termaju tetapi kos penyelenggaraannya juga rendah.

Kertas kerja ini membentangkan hasil awal penciciran membran untuk pemisahan CO<sub>2</sub> dari gas asli menggunakan membran dan projek ini dibiayai oleh IRPA.

Membran polimer yang sesuai untuk pemisahan gas telah disediakan daripada larutan polimer yang dituangkan ke atas lapisan kaca. Teknikk pembalikan fasa digunakan bagi menghasilkan membran asimetrik yang mempunyai kulit nipis di atas lapisan yang porous.

Struktur asimetrik adalah penting untuk keperluan sifat-sifat fluks dan kemimilhan yang tinggi yang diperlukan dalam pemisahan gas. Struktur membran dicirikan dengan menggunakan mikroskop elektron imbasan (SEM). Sel penelapan gas kemudian digunakan untuk mengukur kadar penelapan gas tulen yang melalui membran.

Keputusan awal ke atas pencirian membran menunjukkan bahawa struktur asimetrik telah berjaya dihasilkan dengan mempunyai lapisan nipis atau kulit yang terletak di atas lapisan poros. Walaubagaimanapun untuk mendapatkan pemisahan gas yang lebih baik, ketebalan kulit membran perlu dikurangkan lagi berdasarkan kepada data fluks yang diperolehi.

Kerja-kerja yang sedang berjalan ditumpukan kepada parameter-parameter seperti suhu dan proses sepuh lindap (annealing) yang akan menghasilkan kulit nipis ultra dan lapisan poros.

## INTRODUCTION

The development of membrane for gas separation has been growing rapidly during the last two decades. The first major breakthrough in understanding the selective permeation of gases through nonporous polymer membranes have been proposed by Graham in 1866<sup>1</sup>. Although gas permeation phenomena was discovered since the last century, only in late 1979, this technology has found commercial viability and was widely accepted in a range of industrial, medical and laboratory applications.

The great interest in membrane separation technology<sup>2</sup> is due mainly to the energy efficiency and simplicity of membrane separation devices which make them extremely attractive as a tool for fluid phase separation problems.

There are three key performance attributes that affects membrane economic utility for a particular application<sup>3</sup>. The first is its selectivity, which indicates the ability of the polymer to separate gas species and this characteristic directly affects purity and indirectly affects membrane area. The second is membrane flux or permeability, which is a measure of the capability of the membrane to transport gas species through it. therefore, permeability and selectivity dictates the capital investments or the area of membrane required. The third is the life of membrane, and maintenance and replacement costs. These parameters depend on the type of membrane, and how membrane is packaged into membrane module or permeator.

Membrane technology has been applied succesfully for various gas separation processes<sup>3</sup> such as natural gas sweetening i.e. removed of CO<sub>2</sub> from methane (CH<sub>4</sub>), recovery of CO<sub>2</sub> in enhanced oil recovery (EOR), recovery of H<sub>2</sub> from purge gas in NH<sub>3</sub> production and in refinery operations, recovery of helium from natural gas and oxygen enrichment.

### Membrane properties for Gas Separation

If gas permeation process is to compete with conventional separation techniques in terms of economic viability, the membrane must exhibit certain properties<sup>4</sup>. The most important primary structural properties are its chemical nature, its microcrystalline structure (microcrystalline level), and (on the colloidal level) its pore characteristics (pore size, pore-size distribution and density, and void volume), cell type, and degree of asymmetry. The presence of pores or pinholes in the membrane will greatly reduce, and even destroy, the selectivity for the desired components, because of Knudsen flow or other types of gas transport through such imperfections.

Asymmetric membrane have been prepared from a number of polymers<sup>5</sup>. These membrane possesses an asymmetric cross section, with thin selective layer called skin deposited on top of a porous, non-selective mechanical support, of the same material. For a gas separations, a very dense non-porous skin is required which is pore-free. The most important properties from the functional point of view are permeability and permselectivity<sup>6</sup>. In order to minimize the capital investment and power costs, high permeability and selectivity membrane are required. Without sufficiently high fluxes the membrane areas required would be so large making it uneconomical.

Although these parameter are precisely definable for a given separation process their influence on the overall economic depend on requirements and final specification. For this reason secondary properties<sup>7</sup>, e.g., resistance to compaction, temperature stability, and susceptibility to environmental hazards such as hydrolysis or microbial decomposition, become importance and may even dictate the economics of a given process.

## METHODOLOGY

In the preparation of asymmetric membranes, two techniques have been developed: one utilises the phase inversion process<sup>8</sup> and the other leads to a composite structure by depositing an extremely thin film polymer on a microporous structure. Composite asymmetric membrane<sup>9</sup> is more suitable for reverse osmosis so phase inversion process is utilised for preparation of gas separation membrane.

In phase inversion process a homogeneous polymer solution (cellulose acetate) is cast as thin film on a support, i.e. glass plate followed by the immersion of the film in a non-solvent coagulation bath. In this bath solvent diffuses out of and non-solvent diffuses into the film and polymer will precipitate forming a membrane<sup>10</sup>. Two type of flat sheet membranes were prepared with different coagulation bath compositions. Membrane I was precipitated from water and membrane II from 30% glycerol coagulation bath.

In another method the polymer solution is spun through a spinneret<sup>11</sup> which has an extra outlet for pressurized air or liquid in the centre of the opening, resulting in hollow fiber membranes. A few hollow membranes were prepared by immersing in different concentrations of glycerol.

The membranes produced are heat-treated to obtain varying pore size and structure. A dry asymmetric membranes were obtained when the wet membranes were dried by solvent exchange method<sup>12</sup>.

## MEMBRANE CHARACTERIZATION

### Permeation studies

The gas permeation rate for different type of membrane was measured using 'permeation cell' which is fabricated to measure pure gas permeation rate using flat sheet membrane under a controlled environment. The gas permeability testing apparatus (refer Fig. 7) was filled with a pure gas, namely CO<sub>2</sub> and N<sub>2</sub> from high-pressure cylinders. The highest pressure was 100 psia. The operating temperatures are in range of 25-60°C. Then, by measuring the volumetric flow of gas through the membrane, the gas permeation rate was calculated according to the following equation<sup>3</sup>,

$$P/l = Q/[A(PH-PL)]$$

where  $P/l$  is the permeation rate ( $\text{cm}^3(\text{STP})/\text{cm}^2 \text{ s cm Hg}$ ),  $Q$  is the volumetric flow rate ( $\text{cm}^3/\text{s}$ ),  $A$  is the membrane area ( $\text{cm}^2$ ),  $PH$  and  $PL$  are feed and permeate pressure ( $\text{cm Hg}$ ) respectively, and  $l$  is the membrane thickness.

#### **Determination of the membrane structure**

The membrane morphology was examined using a scanning electron microscope (AMRAY 1830I). After the permeability measurement (flat sheet membrane only), the tested membrane, SEM micrographs of the cross section and both surfaces of the membrane, i.e., skin and support side, were taken. Micrographs were taken of samples coated with a 100-300Å thick gold-palladium film. Fractured samples for SEM observations of the membrane cross section were prepared as follows. A small piece of the tested membrane was cut and conditioned in liquid nitrogen. The membrane was carefully fractured at liquid nitrogen temperature. SEM pictures of the cross section of the fractured samples were taken at 500-650X magnification.

#### **Mechanical studies**

Samples of the membranes (flat sheet) were cut using a dumbbell shaped die and subjected to constant extension-rate tensile experiments at 10 mm/min. These experiments were performed on a tensile tester. The applied force and sample length were recorded as a function of time, and the stress, strain, and elongation, flextural modulus and force at break were calculated.

## **RESULT AND DISCUSSION**

#### **Gas permeation analysis**

The results of permeation rate measurements for pure gases are shown in Table 1, 2, and 3. These tables show the permeation rate of pure gases, carbon dioxide and nitrogen at different feed pressure and operating temperature. Figure 1, 2, 3 show the plots of permeation rate versus feed pressure at various temperature for carbon dioxide and nitrogen. Figures 4, 5, 6 show the dependence of permeation rates of  $\text{CO}_2$  and  $\text{N}_2$  on temperature. The permeation rates of pure  $\text{CO}_2$  and  $\text{N}_2$  increase with increasing temperature. Membrane II allowed nitrogen passed through its matrix but  $\text{CO}_2$  gas was minimum.

#### **Membrane morphology**

##### **Flat sheet membrane**

Figure 8-10 show SEM micrographs of the membrane representing the characteristic morphologies observed in this study. Fig. 8a shows a micrograph cross section of membrane I. As can be seen from this figure, the structure composed mainly of close-cell spongy structure with a thin "skin" at the air-polymer interface. The skin denoted herein represented a thin dense overlayer on top of a thicker and loose sublayer of an integral membrane structure. In case where 30% amount of glycerol is present (membrane II), membrane is formed with macrovoids of finger-like structure. With glycerol as a non-solvent, it is much difficult for water to reach the surface of the polymer film, since the highly viscous glycerol forms a rather impermeable film around the polymer

solution. This causes precipitation to proceed significantly longer, resulting in a thicker top layer and lower flux.

Fig. 9 shows the morphology at the surface facing air. It can be seen that the skin is pore-free which is preferred for gas separation membrane. In contrast, the membrane morphology at polymer-glass interface, as shown in Fig. 10 shows a web-like structure with relatively large pores (about 1 micron) intervening between fibrillar walls.

### Hollow Fiber Membrane

It was found that the microscopic fiber structure (roundness and wall thickness) changed with the spinning parameters used. Initially, it was believed that the irregularity of the fibers was caused by imperfections of the spinnerets (these were still in a development state), but it turned out that with the same spinneret, various forms were obtained. The bore liquid composition had a decisive influence on the final microscopic structure. As can be seen from the cross sections in Figures 11a, 11b, 11c and 11d, the irregular shape on the bore side gets more pronounced when the amount diameter of the fiber hardly changes when more glycerol is added. Addition of glycerol to the bore liquid gives an increase in viscosity. It is possible that the amount of bore liquid has decreased with the increase of glycerol concentration and this affected the formation of nascent membrane. Figure 12a, 12b, 12c and 12d shows the microscopic structure of these membranes. The increasing of glycerol may be the cause of such differences in their structures.

### Mechanical behaviour

The values of stress,  $\sigma_B$ , strain at maximum  $\epsilon_m$ , strain at break,  $\epsilon_B$ , flextural modulus,  $E$ , elongation at maximum,  $\Delta L_m$ , elongation at break,  $\Delta L_B$  and force at break,  $F_B$ , are given in Table 4. These results are indicative of the mechanical properties of membranes I and II. From these results, the membranes are considered mechanically weak. The facts that membrane II contains more of these so called 'macrovoid' as observed in Fig. 8b may be the reason for it to be mechanically weaker than membrane I.

Table 4 shows the machanical properties of Membrane I & II

Sample	$E$ N/mm <sup>2</sup>	$\Delta L_m$ mm	$\epsilon_m$ %	$F_B$ N	$\sigma_B$ N/mm <sup>2</sup>	$\Delta L_B$ mm	$\epsilon_B$ %	Diameter mm
MEM I	94.644	2.213	5.406	5.658	5.217	2.410	5.508	1.128
MEM II	58.746	1.351	8.850	5.213	5.662	1.377	9.638	1.128

### Membrane performance at this stage

Figure 13 shows the performance graph of this project. The permeation rate of Membrane I is compared with the typical values of permeation rates of commercial membrane<sup>3</sup>. From this graph, the permeation rate of nitrogen gas through membrane I is higher than commercial value. For CO<sub>2</sub> gas, the permeation rate of membrane I is lower than commercial membrane. One can make a conclusion from this result that a lot of improvement need to be done to achieve a commercial stage.



## CONCLUSION

Flat sheet and hollow fibre membrane for gas separations were successfully developed having desirable characteristics in terms of morphology and flux performance. However, the membranes developed need improvement in terms of mechanical strength, skin thickness and flux.

## ACKNOWLEDGEMENT

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Table 1: Result of permeation rate measurements of pure carbon dioxide for membrane I

Pressure: 70 Psia	
Temperature	Permeation rate [cm <sup>3</sup> (STP)/cm <sup>2</sup> .s.cmHg]
25	1.9354 x 10 <sup>-4</sup>
30	3.4866 x 10 <sup>-4</sup>
35	3.1602 x 10 <sup>-4</sup>
40	3.8788 x 10 <sup>-4</sup>
45	3.6064 x 10 <sup>-4</sup>
50	5.9196 x 10 <sup>-4</sup>
60	7.6795 x 10 <sup>-4</sup>
Pressure: 90 Psia	
Temperature	Permeation rate [cm <sup>3</sup> (STP)/cm <sup>2</sup> .s.cmHg]
25	4.3355 x 10 <sup>-5</sup>
30	6.1658 x 10 <sup>-5</sup>
35	7.0872 x 10 <sup>-5</sup>
40	1.0197 x 10 <sup>-4</sup>
45	1.1927 x 10 <sup>-4</sup>
50	1.3194 x 10 <sup>-4</sup>
55	1.6709 x 10 <sup>-4</sup>
60	2.099 x 10 <sup>-4</sup>
Pressure: 100 Psia	
Temperature	Permeation rate [cm <sup>3</sup> (STP)/cm <sup>2</sup> .s.cmHg]
25	3.3091 x 10 <sup>-6</sup>
30	3.9777 x 10 <sup>-6</sup>
35	4.4863 x 10 <sup>-6</sup>
40	4.7054 x 10 <sup>-6</sup>
45	4.4483 x 10 <sup>-6</sup>
50	4.4795 x 10 <sup>-6</sup>
55	4.7225 x 10 <sup>-6</sup>
60	6.6450 x 10 <sup>-6</sup>

Table 1: Result of permeation rate measurements of pure nitrogen for membrane I

Pressure: 70 Psia	
Temperature	Permeation rate [cm <sup>3</sup> (STP)/cm <sup>2</sup> .s.cmHg]
25	2.0708 x 10 <sup>-4</sup>
30	3.8826 x 10 <sup>-4</sup>
35	1.3179 x 10 <sup>-3</sup>
Pressure: 80 Psia	
Temperature	Permeation rate [cm <sup>3</sup> (STP)/cm <sup>2</sup> .s.cmHg]
25	1.5532 x 10 <sup>-4</sup>
30	5.0982 x 10 <sup>-4</sup>
35	1.2301 x 10 <sup>-3</sup>
Pressure: 90 Psia	
Temperature	Permeation rate [cm <sup>3</sup> (STP)/cm <sup>2</sup> .s.cmHg]
25	6.3671 x 10 <sup>-5</sup>
30	3.3847 x 10 <sup>-4</sup>
35	2.1515 x 10 <sup>-3</sup>
Pressure: 100 Psia	
Temperature	Permeation rate [cm <sup>3</sup> (STP)/cm <sup>2</sup> .s.cmHg]
25	3.0000 x 10 <sup>-4</sup>
30	4.4748 x 10 <sup>-4</sup>
35	1.1672 x 10 <sup>-3</sup>



Table 3: Result of permeation rate measurements of pure nitrogen for membrane I

Pressure: 36 Psia	
Temperature	Permeation rate [cm <sup>3</sup> (STP)/cm <sup>2</sup> .s.cmHg]
70	8.86 x 10 <sup>-6</sup>
80	6.24 x 10 <sup>-6</sup>
90	5.63 x 10 <sup>-6</sup>
100	6.10 x 10 <sup>-6</sup>
Pressure: 46 Psia	
Temperature	Permeation rate [cm <sup>3</sup> (STP)/cm <sup>2</sup> .s.cmHg]
70	13.412 x 10 <sup>-6</sup>
80	12.81 x 10 <sup>-6</sup>
90	10.44 x 10 <sup>-6</sup>
100	9.10 x 10 <sup>-6</sup>
Pressure: 61 Psia	
Temperature	Permeation rate [cm <sup>3</sup> (STP)/cm <sup>2</sup> .s.cmHg]
70	19.89 x 10 <sup>-6</sup>
80	18.22 x 10 <sup>-6</sup>
90	16.10 x 10 <sup>-6</sup>
100	14.75 x 10 <sup>-6</sup>

Figure 1: Effect of pressure on permeation rate of pure CO<sub>2</sub> for Membrane I

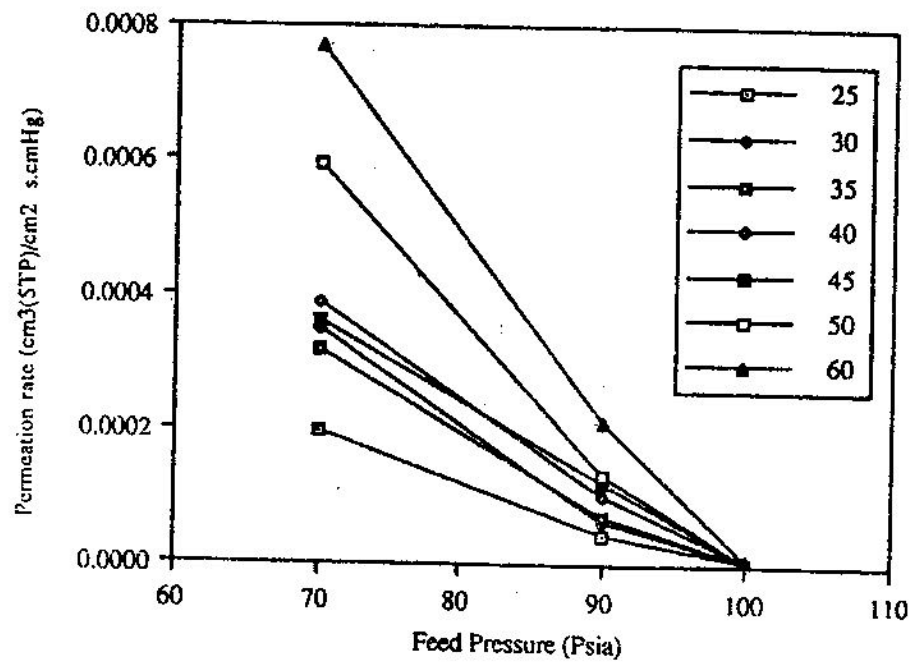


Figure 2: Effect of pressure on permeation rate of pure CO<sub>2</sub> for Membrane I

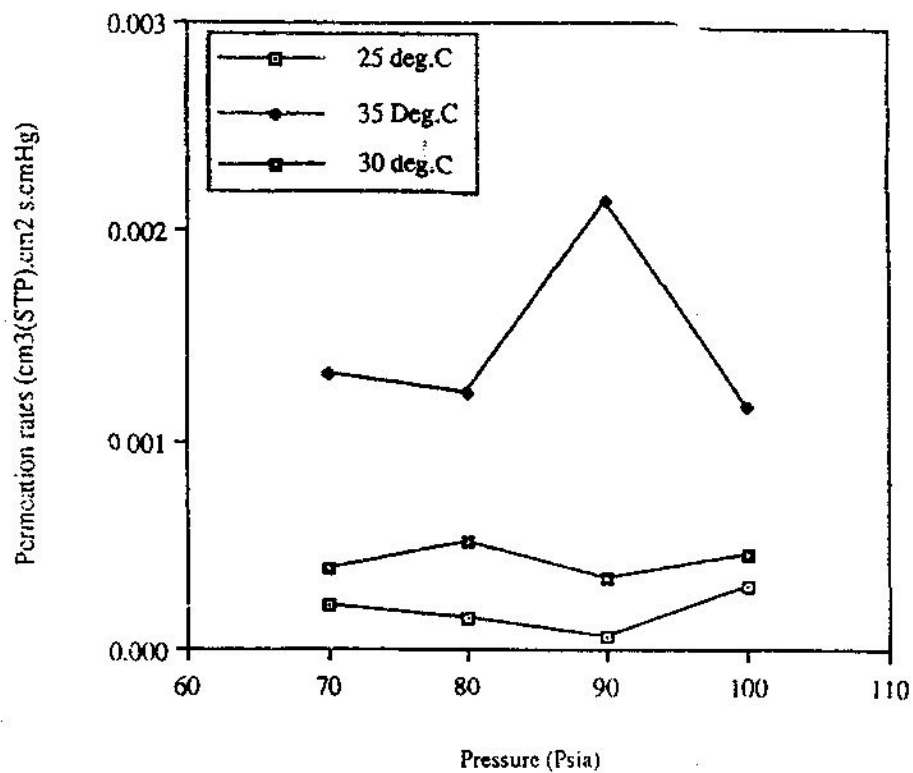


Figure 3: Effect of pressure on permeation rate of pure nitrogen for Membrane II

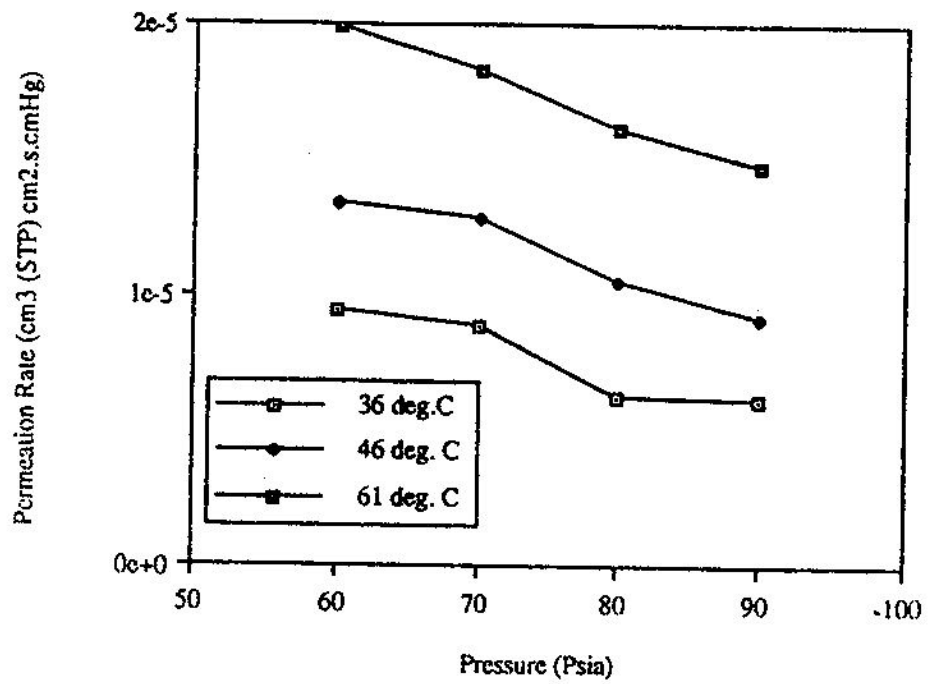


Figure 4: Effect of temperature on permeation rate of pure CO<sub>2</sub> for Membrane I

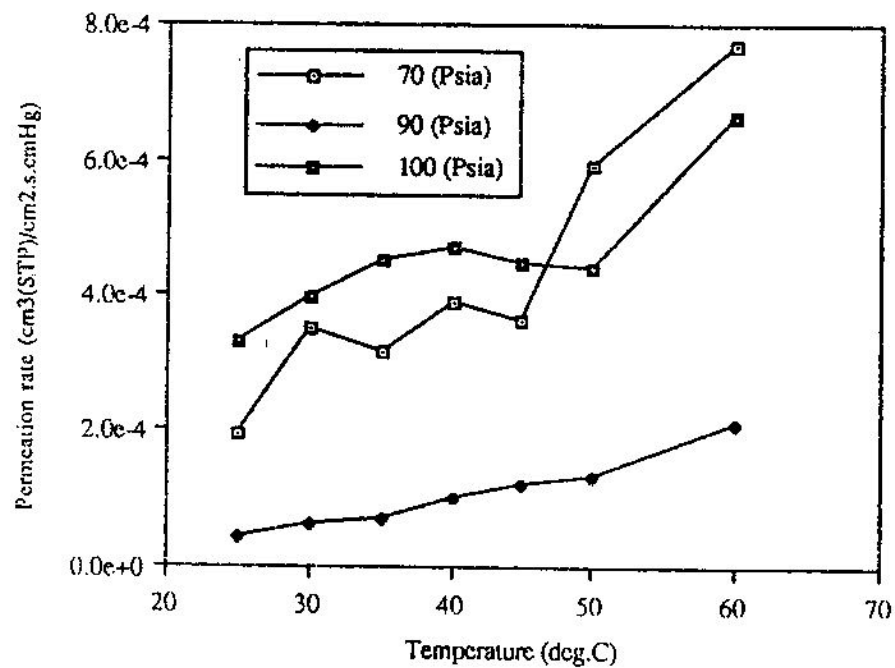


Figure 5: Effect of temperature on permeation rate of pure nitrogen for Membrane I

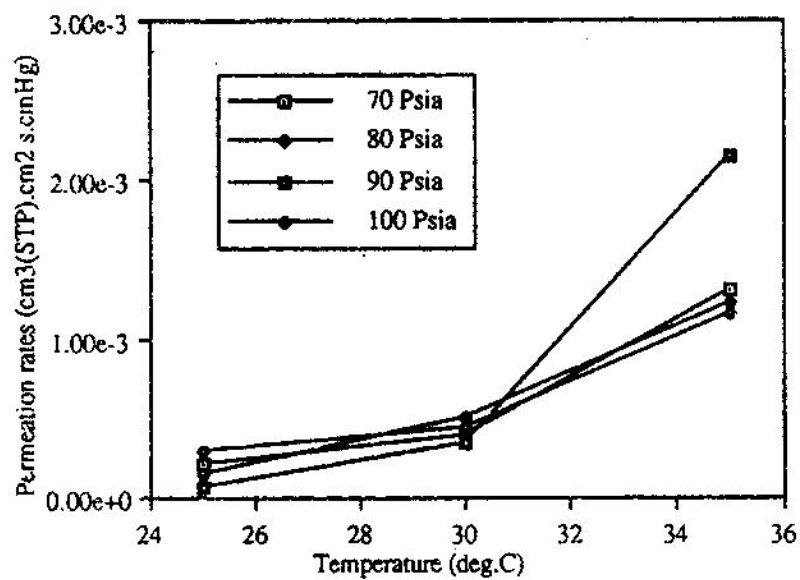
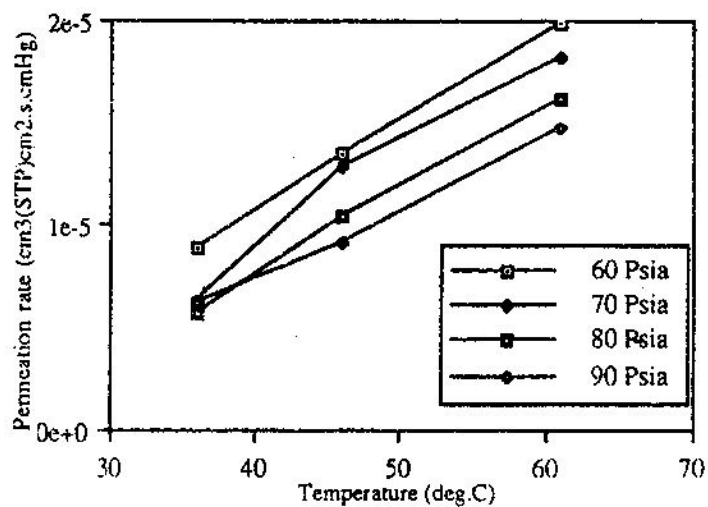


Figure 2: Effect of temperature on permeation rate of pure nitrogen for Membrane II



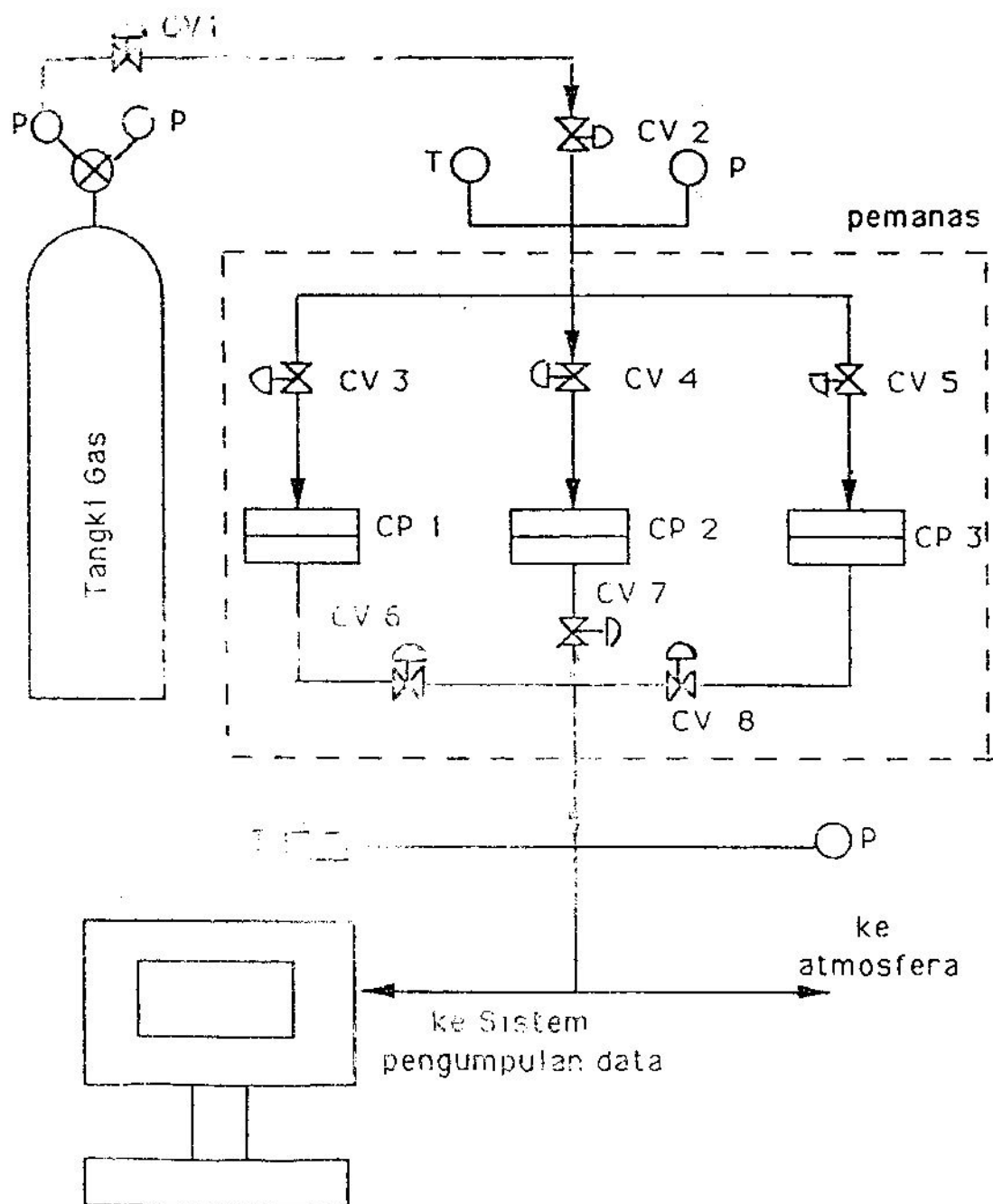
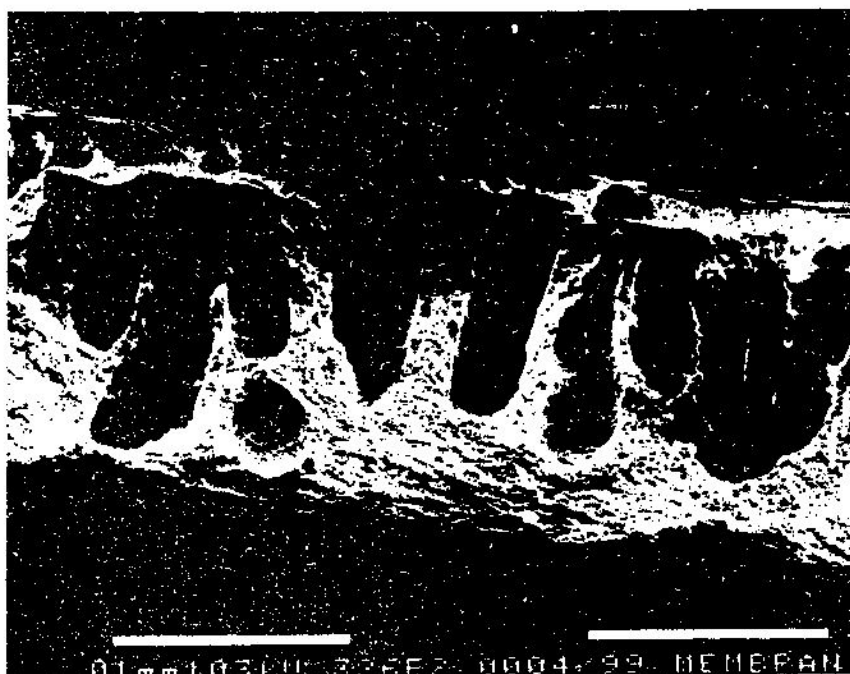


Figure 7: Schematic diagram of Permeation Cell (using flat sheet membrane module)



(a)



(b)

Figure 8: Cross sections of flat asymmetric gas separation membranes coagulated in different type of bath

a) water

b) 30%



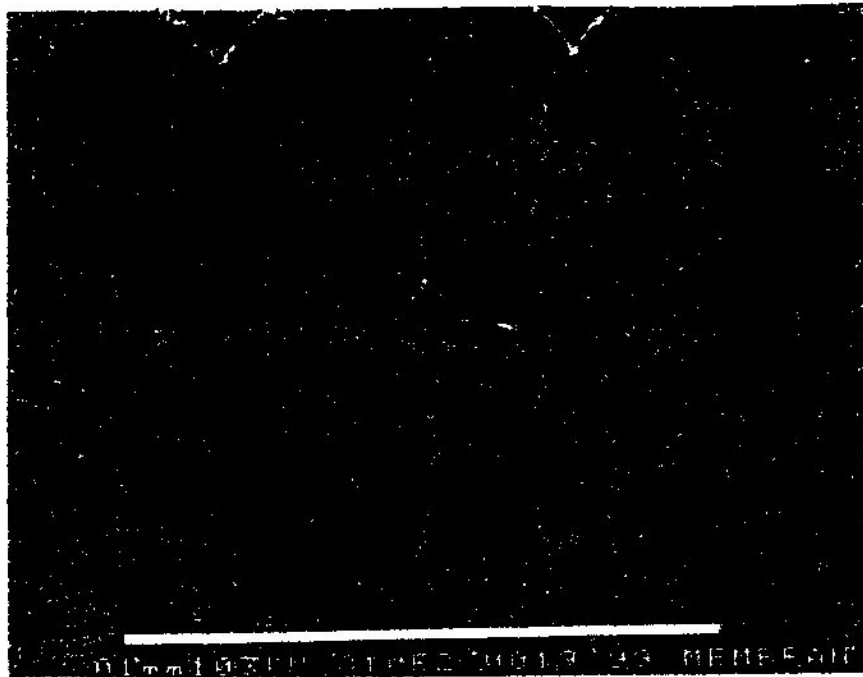


Figure 9: Scanning electron micrographs of surface facing air

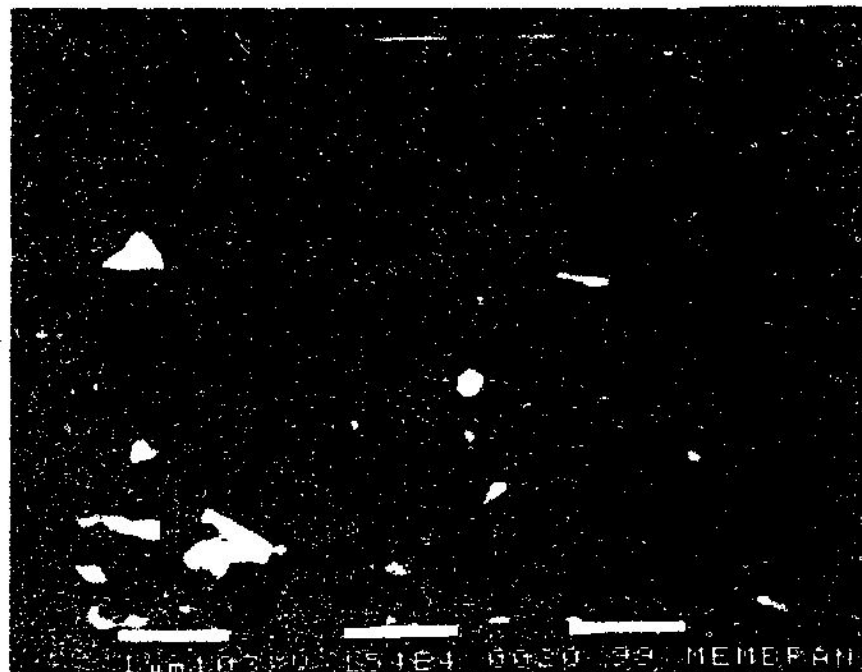
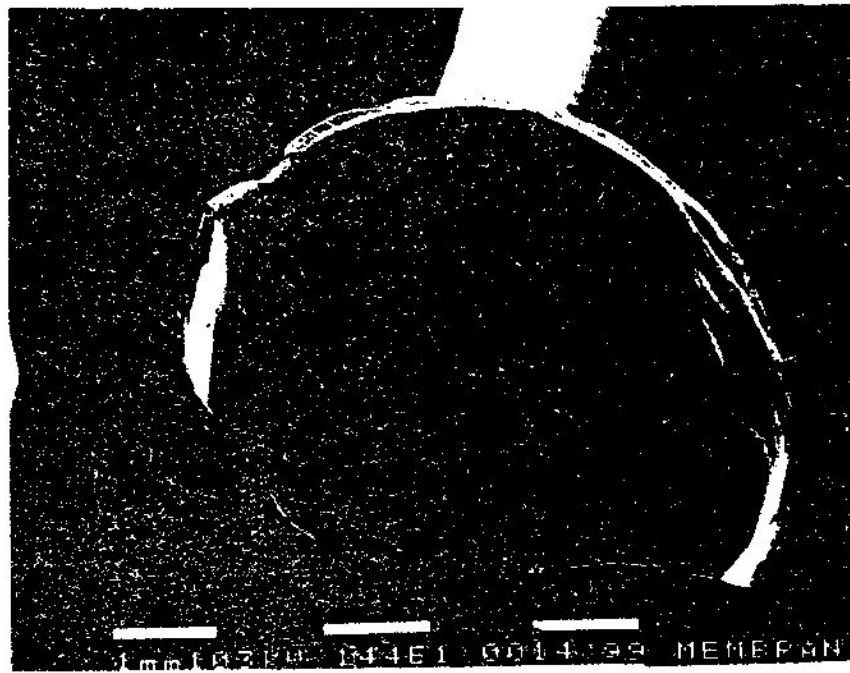


Figure 10: Scanning electron micrographs of surface facing glass



(a)

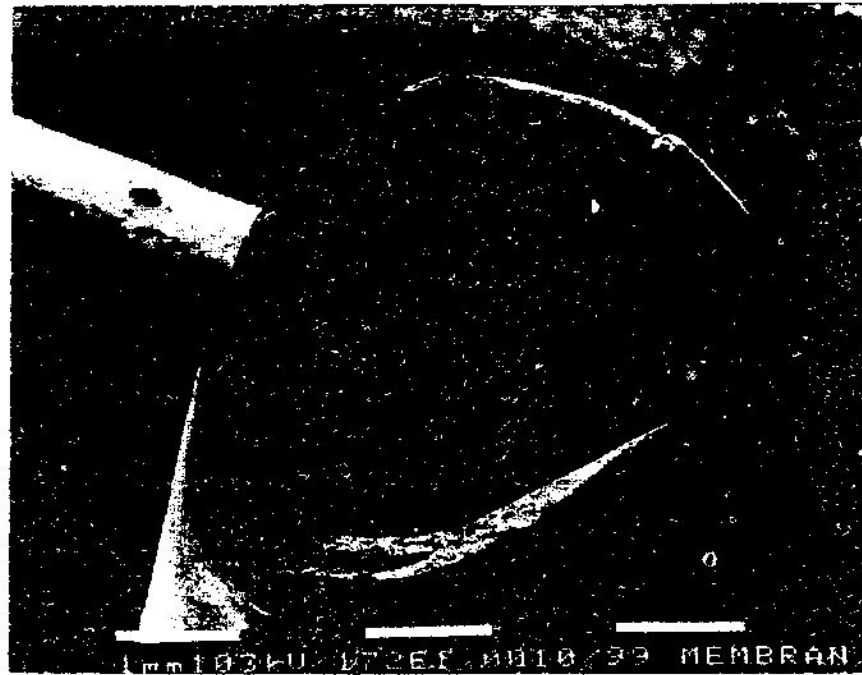


(b)

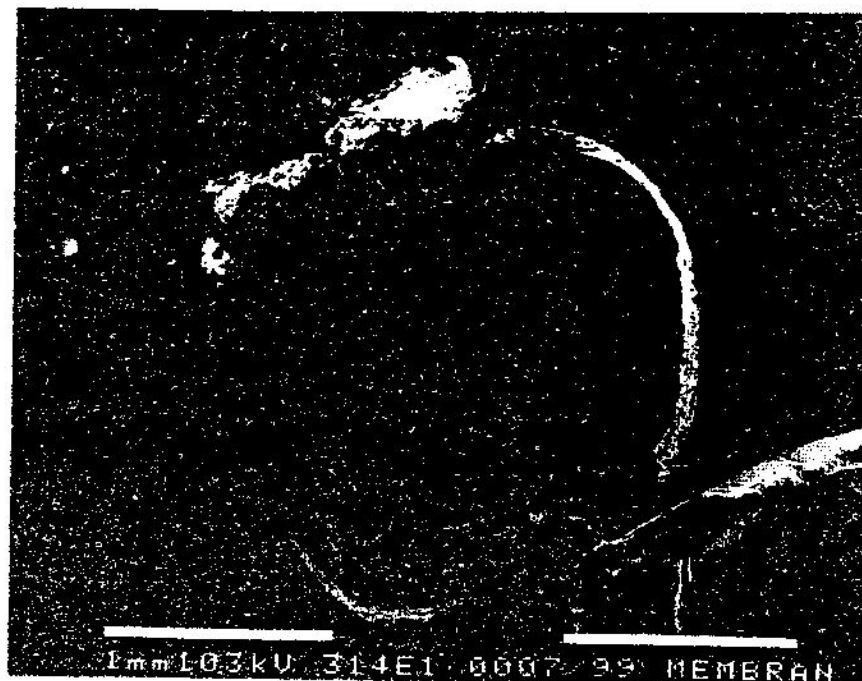
Figure 11: Cross sections (macroscopic structures) of hollow fibers, spun with various amounts of glycerol in the bore liquid

a) 5%

b) 10%



(c)

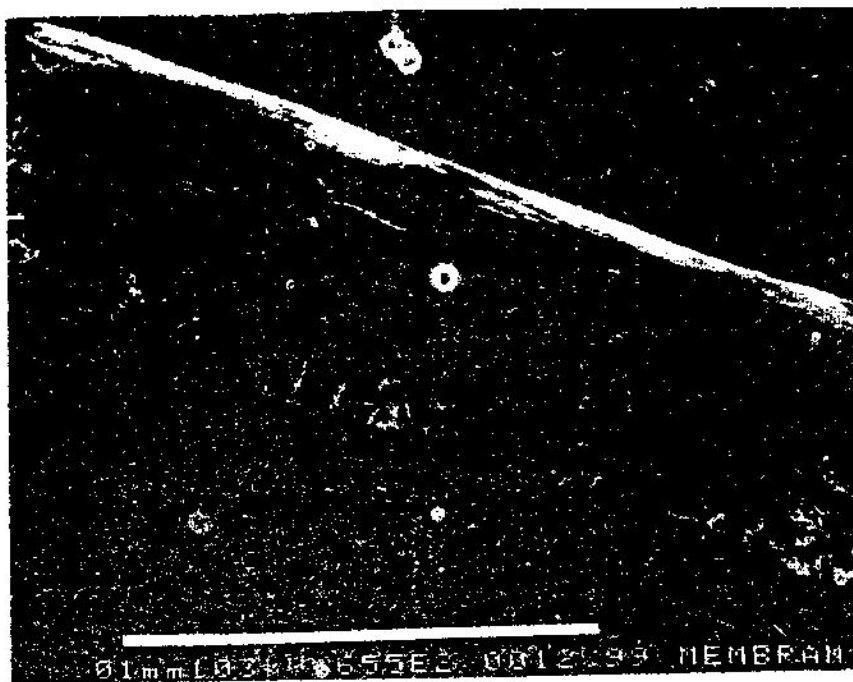


(d)

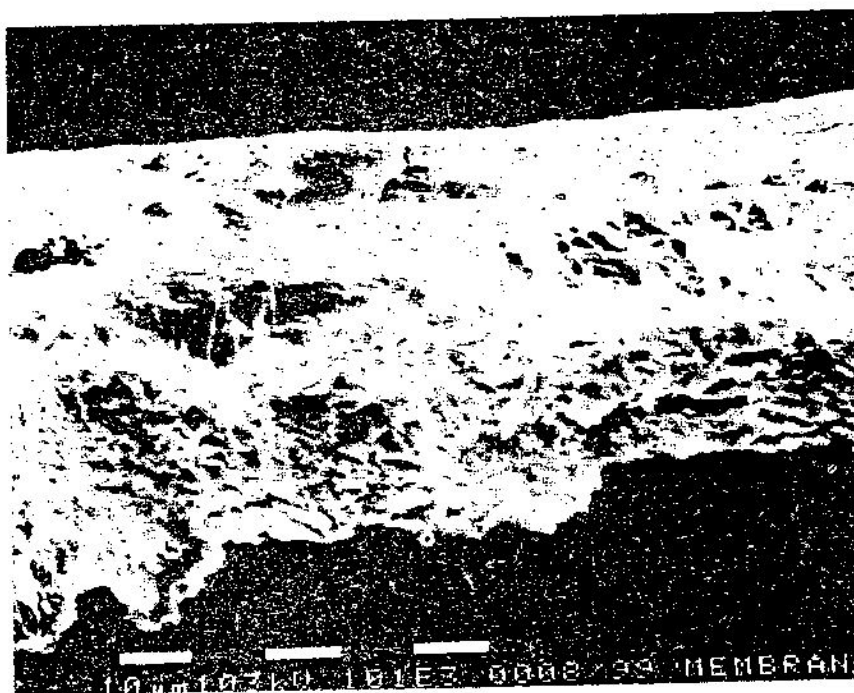
Figure 11: Cross sections (macroscopic structures) of hollow fibers, spun with various amounts of glycerol in the bore liquid

c) 15%

d) 20%



(c)



(d)

Figure 12: Cross sections (macroscopic structures) of hollow fibers, spun with various amounts of glycerol in the bore liquid

c) 15%

d) 20%



(c)



(d)

Figure 12: Cross sections (macroscopic structures) of hollow fibers, spun with various amounts of glycerol in the bore liquid

c) 15%

d) 20%

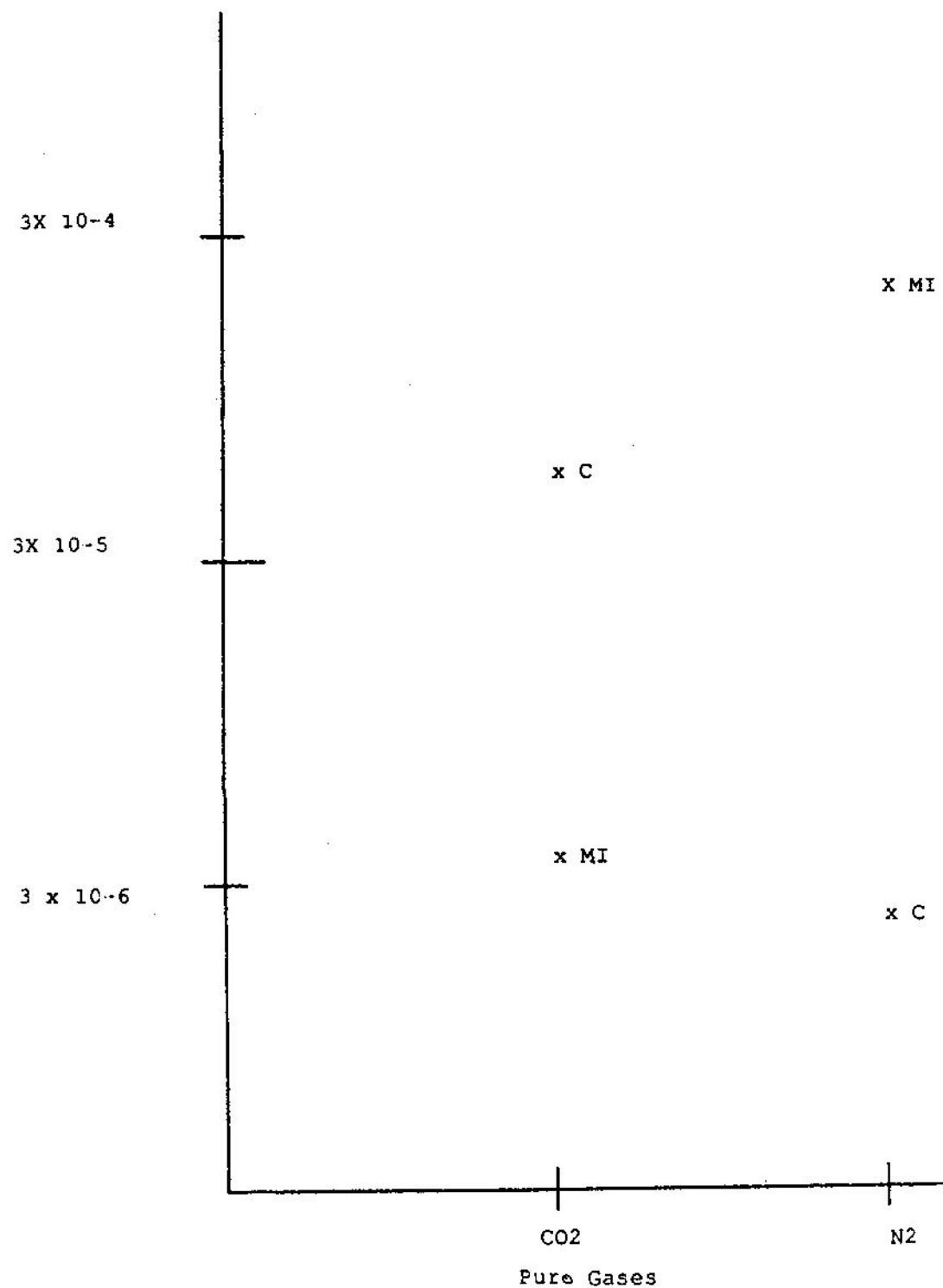


Figure 13: The performance of Membrane I compared to the commercial membrane  
 C = Commercial Membrane  
 M1 = Membrane I (at Pressure = 100 Psia, Temperature = 25 deg. C)