

일본에서의 기체분리막의 현황 및 응용

(일본 명치대학교 공화과)

Nakagawa

APPLICATIONS AND A VIEW OF GAS SEPARATION BY MEMBRANES IN JAPAN

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I. INTRODUCTION

The development of separation technology is an important research subject as is clear from its role in the Japanese government's research and development program for basic technology for the next generation (1981 ~ 1990). Japan is poor not only in mineral resources but also in energy resources and if a sudden change occurs in oil producing facility or an accident occurs in a nuclear power plant, then energy policy must undergo changes and economic foundations may collapse. Japan has already experienced this. Although, oil prices are stable at present and Japan can import oil at low cost due to the yen appreciation, Japan needs to promote development work for any new energy crisis that may come in the future. This has been the motive for gas separation membrane development in Japan. The study of gas permeation through polymer membranes, which is the basis for membranes for gas separation, at Japanese universities began many years ago, but interest in membranes for gas separation was aroused mainly by the Government. The development of gas separation membranes in Japan started with membranes for oxygen separation on an industrial scale. As far as energy conservation is concerned, burning fuel in the presence of gas other than oxygen, i.e., nitrogen, in a large quantity reduces the combustion efficiency. On the other hand, nitrogen enriched air containing more than 95 % nitrogen is in great demand from the semiconductor production industries. The development work on hydrogen separation membranes has been successfully conducted under MITI's large scale project (MITI: Ministry of International Trade and Industry). This three-year project started in April 1979 under the title "Gas separation/refining technology" as a sub-theme of the "Production Processes for Basic Chemicals from Carbon Monoxide". Mixture of hydrogen and carbon monoxide is called "synthetic gas" from which many chemicals can be synthesized. The membrane was requested to have a high separation factor for the hydrogen/carbon monoxide mixture at elevated temperature, e.g. more than 100 °C.

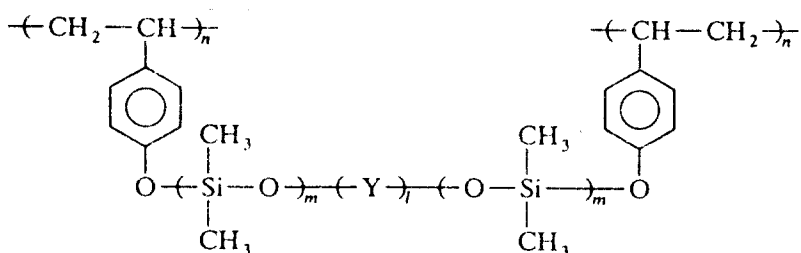
Now, another large project just started in January 1992 for developing carbon dioxide separation membranes for reducing the concentration of carbon dioxide in combustion gas.

In the first section in this chapter, transport properties of the new membranes for industrial application that have been developed in Japan will be explained in detail. This will be followed in the second section by a discussion on their industrial application for gas separation.

II. RECENT PROGRESS OF MEMBRANES FOR GAS SEPARATION IN JAPAN

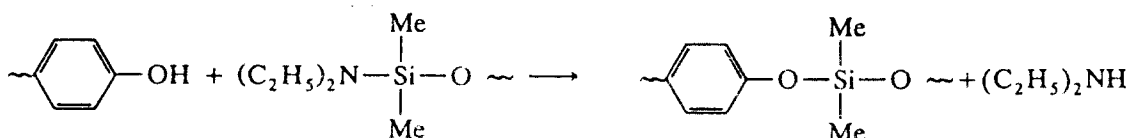
A. Polydimethylsiloxane-polyvinylphenol block copolymer membranes

Permeability coefficients of polydimethylsiloxane (PDMS) to light gases like H_2 , O_2 , N_2 are very high though separation factors are very low. However, it is very difficult to prepare ultra thin membranes with thickness as low as $0.1\mu m$, because of poor mechanical properties of this rubbery polymer. High flux or high permeance of oxygen through membranes, expressed as P/ℓ , is required for combustion. Matsushita Electric Co. has developed block copolymers of poly(hydroxystyrene) and PDMS, known as "HS-POLYMER". Very thin membranes can be obtained through sacrifice of only a small amount of intrinsic permeability.



block copolymer of poly(hydroxystyrene) and PDMS

The chemical reaction of diethylamino groups, which exit at the ends of PDMS chains, with the hydroxyl groups of phenol was used:



The extent of dimethylsiloxane introduced was controlled by using poly(vinylphenol) where some hydroxyl groups in the poly(vinyl phenol) were capped by trimethylsilanol. The block copolymers thus obtained dissolve in cyclic ethers such as tetrahydrofuran (THF). The effect of the content of the dimethylsiloxane component on the oxygen permeability is shown in Fig.1 [1]. As can be seen, the oxygen permeability drastically increases around 50~60 % siloxane content. According to Barnabeo and co-workers[2], permeability coefficients of random copolymers can be expressed as follows:

$$\log P_{1,2} = V_1 P_1 + V_2 P_2 \quad (1)$$

where, $P_{1,2}$ and P_2 are permeability coefficients of copolymer membranes, homopolymers 1 and 2 in the copolymer. For block copolymers, the relationship between volume % and gas permeability coefficients from different curves which depend on the morphology of the phases. In the case where polymer 1 forms a continuous phase and polymer 2 forms a dispersed phase, the permeability coefficient of the copolymer will follow eq.(2).

$$P_{1,2} = P_1 \frac{P_2 + 2P_1 - 2V_2(P_1 - P_2)}{P_2 + 2P_1 + V_2(P_1 - P_2)} \quad (2)$$

A comparison of the gas permeabilities of random copolymers

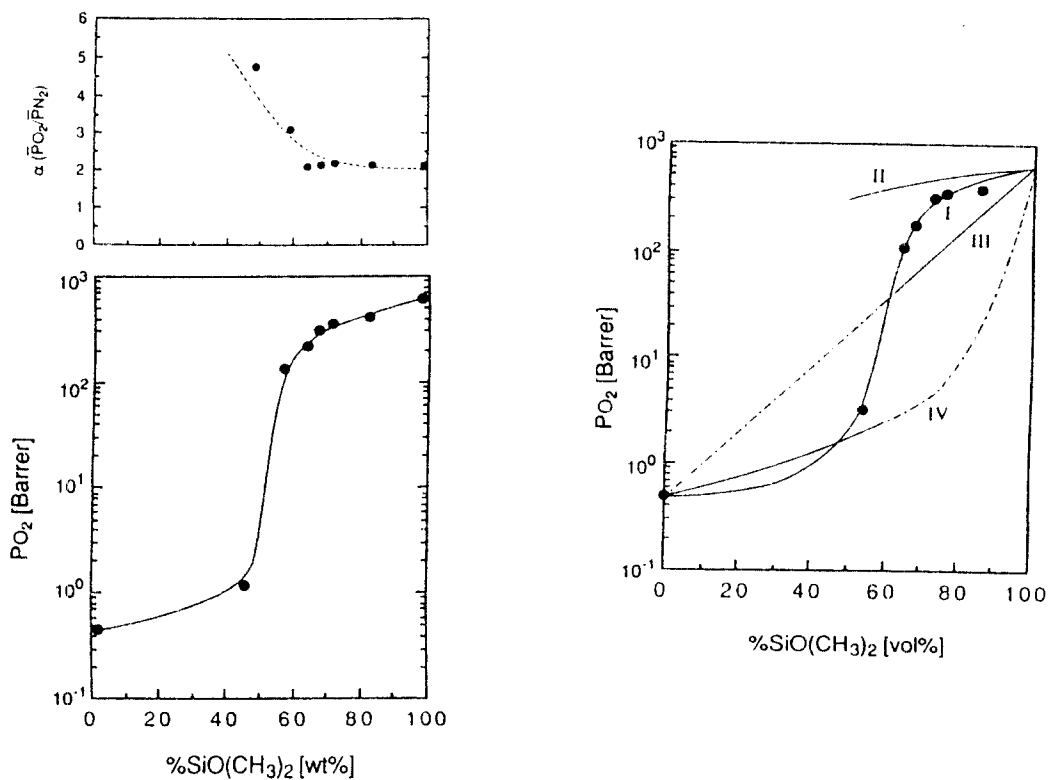


FIGURE 1. Effect of dimethylsiloxane content in copolymer membranes of dimethylsiloxane with hydroxystyrene on the oxygen permeability and the separation factor for O_2/N_2 .

FIGURE 2. Comparison of experimental data with theoretical values of oxygen permeability for copolymer membranes of hydroxystyrene and dimethylsiloxane: (I) experimental data; (II) calculated values, using oxygen permeability of poly(dimethyl siloxane) and volume fraction of dimethylsiloxane in the copolymer; (III) calculated values using Equation 1; (IV) calculated values using Equation 2.

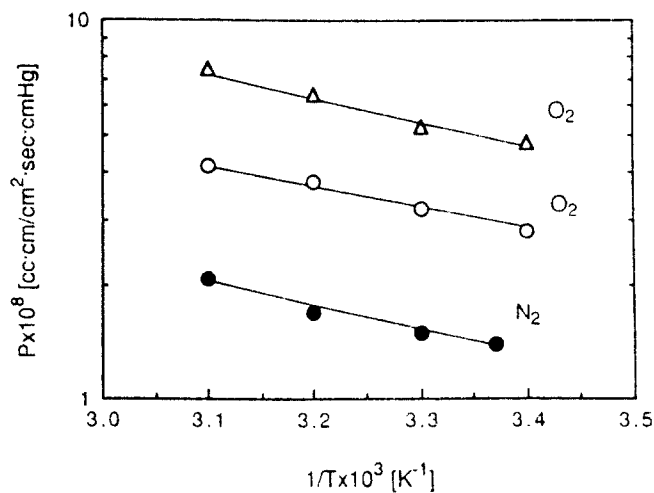
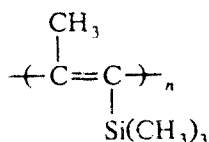


FIGURE 3. Comparison of Arrhenius plots of gas permeability of the copolymer membrane of dimethylsiloxane with hydroxystyrene.

with block copolymers are shown in Fig.2. Thus, the PDMS component in the highly permeability copolymers shown in Fig.2 forms the continuous phase. Arrhenius plots comparing these copolymers with PDMS are shown in Fig.3. The membranes were prepared using the water surface spreading method, illustrated in Fig.4[3]. The ultrathin copolymer membranes can be prepared in the form of laminated composite membranes.

B. Modified poly[1-(trimethylsilyl)-1-propyne] membranes

Many membrane researchers are devoting attention to a new polymer, poly[1-(trimethylsilyl)-1-propyne], PMSP or PTMSP, which was first synthesized in Japan [4]. The gas permeability coefficients for PMSP membranes at the time of manufacture are the highest of all polymeric membranes, as shown in Fig.5. PMSP is a glassy polymer at ambient temperature. The high gas permeability of PMSP results in part from substantial gas solubility, which appears to be due, in tern, to the large free volume of this glassy polymer[5]. The structure of PMSP, which consists



PMSP

of relatively rigid backbone chains separated by bulky trimethylsilyl side groups, is probably responsible for this large free volume. The typical data for permeability, diffusivity and solubility coefficients are summarized in Table 1 [6]. The biggest problem with the PMSP membrane is the deterioration of its high permeability with the passage of time or thermal hysteresis. The deterioration of its gas permeability strongly depends on the thickness of the membrane. If the thickness is less than $1\mu\text{m}$ and the membrane is kept in a vacuum vessel, the gas permeability coefficient is reduced to the order of 10^{-9} in a few hours [7]. Much effort is now being devoted to solving this problem by the lamination of a ultrathin membrane with less permeable property or the formation of more dense layer on the surface of the PMSP membrane. Another problem of PMSP membranes is their very low separation factors. In order to improve the separation factor, fluorination on the surface of the membranes was investigated in the USA [8]. The main reasons for the deterioration are physical aging of thick membranes which appear in a relatively long time and absorption of oily vapors for ultrathin membranes which occurs in a very short time.

Modification by filling with relatively non-volatile materials is very effective in reducing the Langmuir sorption mode, as well as sorption of oily vapors. Filling with only few percent of the PDMS oligomer is enough for stabilization. Effect of the content of PDMS oligomer and poly[1,3,5-tris(3,3,3-trifluoropropyl)-1,3,5-trimethyl cyclotrisiloxane], PTFMS, on the permeability of oxygen and nitrogen is shown in Fig.6 [9]. The effect of modified PMSP membranes on the thermal hysteresis is shown in Fig.7 [9]. The added PDMS may exist in glassy microvoids in PMSP.

We have found that composite membranes, which consist of laminated thin PMSP layer and porous polypropylene, Duragard 2400, have a relatively better separation factor for oxygen and nitrogen mixtures. The model structure of the composite

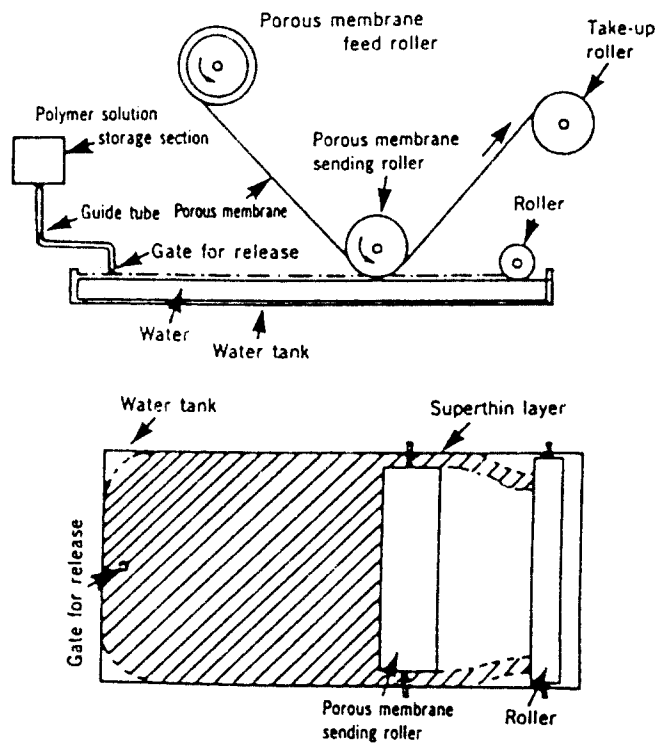


FIGURE 4. Water surface spreading method for preparing ultrathin membranes.

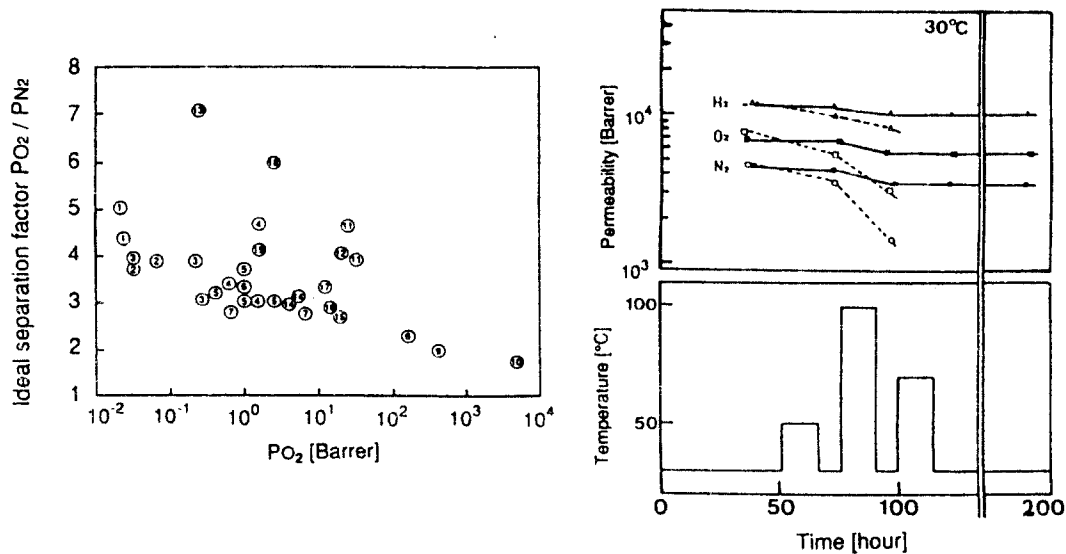


FIGURE 5. Relationship between permeability coefficient of oxygen and ideal separation factors to nitrogen in various polymers. 1, Poly(ethylene terephthalate); 2, Nylon-6; 3, poly(vinyl chloride); 4, polycarbonate; 5, polyethylene; 6, poly(propylene); 7, cellulose; 8, poly(dimethylsiloxane)-polycarbonate block copolymer; 9, poly(dimethylsiloxane); 10, poly[1-(trimethylsilyl)-1-propyne]; 11, poly(4-methyl pentene-1); 12, poly(2,6-dimethylphenylene oxide); 13, poly(vinyl acetate); 14, Teflon-FEP; 15, natural rubber; 16, polybutadiene; 17, ethyl cellulose; 18, polystyrene; 19, butyl rubber.

FIGURE 7. Thermal hysteresis of gas permeability of PMSP/PDMS (99.3/0.7) and PMSP membrane. All measurements of the gas permeability were carried out at 30°C: (---) PMSP; (—) PMSP filled with PDMS oligomer.

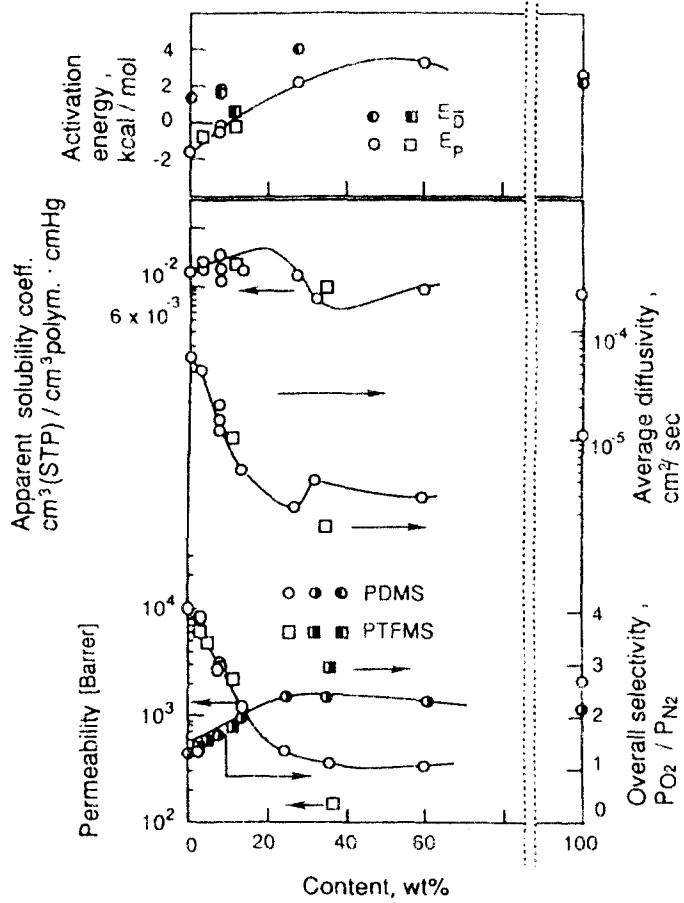


FIGURE 6. Effect of siloxane content of PDMS- and/or PTFMS-filled PMSP membrane on gas permeability, diffusivity, and solubility.

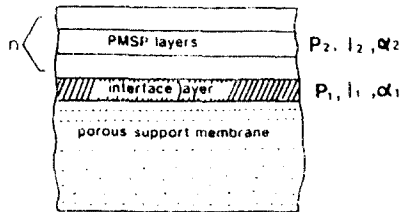


FIGURE 8. Structure of model composite membrane of PMSP with porous support.

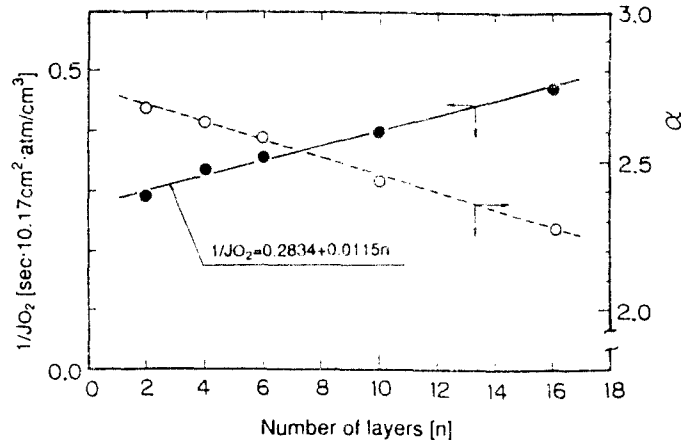


FIGURE 9. Variation of $1/J_{O_2}$ (●) and α (○) with the number of PMSp layers in composite membrane.

TABLE 1
Permeability (*P*), Effective Diffusion (*D*),
and Solubility Coefficient (*S*) of PMSP at 30°C

| Gas | <i>P</i> (barrer) | <i>D</i> × 10 ⁵ (cm ² / s) | <i>S</i> × 10 ³ (cm ³ (STP) / (cm ³ polymer)) |
|-----------------|----------------------|---|---|
| He | 5,080 | | |
| H ₂ | 13,200 | 68.9 | 1.91 |
| Ne | 3,290 | 10.2 | 3.23 |
| O ₂ | 7,730 | 3.58 | 21.6 |
| Ar | 6,900 | 2.65 | 26.3 |
| CH ₄ | 13,000 | 2.27 | 57.3 |
| N ₂ | 4,970 | 2.55 | 19.5 |
| CO ₂ | 28,000 | 2.17 | 129 |
| Kr | 9,080 | 1.33 | 68.3 |
| Xe | 11,700 | 0.443 | 264 |

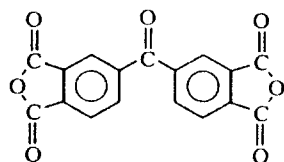
TABLE 2
Gas Transport Properties of Typical Polyimide Membranes

| Membrane material | <i>P</i> _{H₂} ^a | | <i>P</i> _{N₂} ^a | | <i>P</i> _{H₂} / <i>P</i> _{N₂,CO} ^b | | <i>E_p</i> ^c | |
|-------------------|--|-------|--|-------|---|-------|-----------------------------------|-----------------------|
| | 30°C | 100°C | 30°C | 100°C | 30°C | 100°C | (H ₂) | (N ₂ , CO) |
| Kapton | 2.0 | 7.5 | 0.027 | 0.135 | 74.0 | 55.6 | 4.24 | 5.17 |
| BTDA-DADE | 0.8 | 3.5 | 0.0055 | 0.056 | 145.0 | 63.0 | 4.74 | 7.41 |
| BDA-DADE | 25 | 120 | 0.29 | 1.80 | 86.2 | 66.7 | 4.62 | 5.37 |
| TCDA-DADE | 13 | 37 | 0.082 | 0.42 | 158.5 | 88.1 | 3.33 | 5.98 |

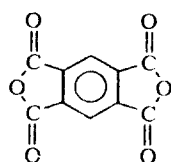
^a Unit of permeability coefficients: barrer.
^b Ratio of permeability coefficient.
^c Apparent activation energy for permeation.

TABLE 4
Gas Permeability of Various New Copolyimide Membranes

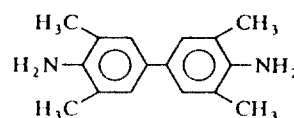
| Composition of polyimide (millimoles) | | | | | | °C | Gas permeability <i>P</i> (barrers) | | | | | |
|---------------------------------------|------|------|------|---------|------|----|-------------------------------------|-----------------|----------------|----------------------------------|-----------------------------------|---------------------------------|
| Carboxylic dianhydride | | | | Diamine | | | H ₂ | CO ₂ | O ₂ | H ₂ / CH ₄ | CO ₂ / CH ₄ | O ₂ / N ₂ |
| BPDA | BTDA | PMDA | 6FDA | TMBD | MTMB | | | | | | | |
| — | — | — | 21 | 21 | — | 30 | 134 | 80.5 | 30.8 | 60 | 36 | 4.2 |
| — | — | — | 21 | — | 21 | 30 | 106 | 51.2 | — | 73 | 35 | — |
| — | 21 | — | — | — | 21 | 30 | 44.4 | 18.6 | 46.5 | 75 | 32 | 5.3 |
| — | — | 21 | — | — | 21 | 30 | 48.7 | 19.5 | — | 95 | 38 | — |
| 2.1 | — | — | 18.9 | 21 | — | 30 | 124 | 72 | — | 62 | 36 | — |
| 6.3 | — | — | 14.7 | 21 | — | 30 | 111 | 64.9 | — | 60 | 35 | — |
| — | — | 2.1 | 18.9 | 21 | — | 30 | 124 | 96.2 | — | 51 | 39 | — |
| — | — | 4.2 | 16.8 | 21 | — | 30 | 150 | 103 | — | 43 | 30 | — |
| — | — | 10.5 | 10.5 | 21 | — | 30 | 127 | 82 | — | 49 | 32 | — |



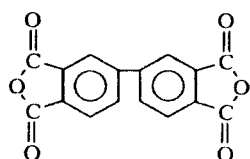
BTDA



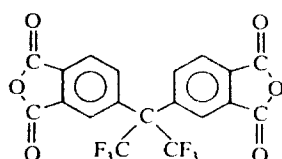
PMDA



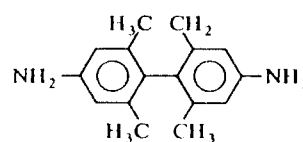
TMBD



BPDA



6FDA



MTMB

membrane is given in Fig.8. In this model, if the resistivity for the transport of a gas through the porous membrane is neglected, the following equations are obtained for the flux of oxygen, J_{O_2} , and the separation factor for O_2/N_2 , α , of the composite membrane:

$$J_{O_2} = \Delta p \{ (n \ell_2 / P_2) + (\ell_1 / P_1) \}^{-1} \quad (3)$$

$$\alpha = \alpha_1 + (\alpha_1 - \alpha_2) [(\ell_1 / P_1) / \{ (n \ell_2 / P_2) + (\ell_1 / P_1) \}] \quad (4)$$

where; P_1 , α_1 and ℓ_1 represent oxygen permeability, separation factor and thickness of the interface layer(1), respectively; P_2 , α_2 and ℓ_2 are the oxygen permeability, separation factor and thickness of a PMSP layer(2), respectively; n is the number of layers of PMSP and Δp is the pressure difference across the composite membrane.

The reciprocal value of J_{O_2} will be proportional to the number of layers of PMSP, n , if the interface layer remains invariant to the number of layers of PMSP:

$$1/J_{O_2} = n(\ell_2 / P_2)(1/\Delta p) + (\ell_1 / P_1)(1/\Delta p) \quad (4)$$

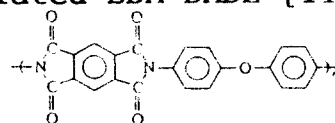
Experimental results are shown in Fig.9. The plot of $1/J_{O_2}$ versus n was found to be a good straight line which agreed with the calculated one when $\alpha_2=1.4$; $\ell_2=40$ nm; membrane area $A=10.17$ cm²; and $\Delta p=76$ cmHg. Also, α agreed well with the calculated curve. The values of ℓ_1/P_1 and α_1 of the interface layer were found to be as 212 cm²·s·cmHg cm⁻³ and 2.83 from the above results, respectively[7]. Perhaps, there might be present a more dense layer in the intersurface between PMSP and Duragard.

For practical use of the layered PMSP membrane, an additional thin layer of PDMS block copolymer, which was mentioned in a previous section, is laminated on the top layer to prevent absorption of oily vapors. Such layered composite type membranes have been used to produce oxygen enriched air for combustion as shown in the next section.

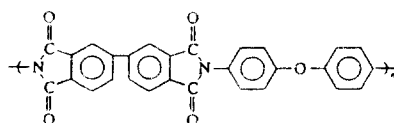
C) Polyimide membranes developed in Japan

Three typical kinds of polyimide membranes are shown in Table 2. As is well known, polyimide is synthesized from a tetracarboxylic dianhydride and a diamine. Originally, diamino diphenyl ether(DADE) was used as in the case of Kapton^R. Ube Industries developed a new polyimide, Upilex^R, composed of biphenyl tetracarboxylic dianhydride(BPDA) and DADE, abbreviated BPDA-DADE and a modified polyimide with diaminodiphenyl methane (DADM) as a copolyimide, BPDA-DADE, DADM [10]. This polyimide has two phenyl groups in one acid component. Therefore, the stacking effect between aromatic rings should be stronger than that of Kapton^R. This makes the intersegmental distance shorter. On the contrary, Nitto Electric Co. developed a polyimide membrane composed of butane tetracarboxylic dianhydride (BDA) and DADE, abbreviated BDA-DADE [11].

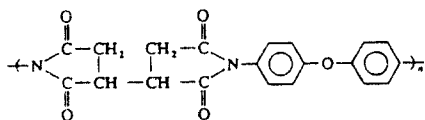
Kapton^R



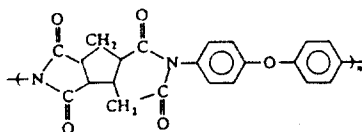
BPDA-DADE



BDA-DADE



TCDA-DADE



The thermal movement of alkyl groups is considered to be much easier than the aromatic rings in the main chain of BDA-DADE, which causes high diffusivity. It is interesting to note, that the permeability coefficients of the polyimide containing cyclic hydrocarbon in the main chain composed of 2,3,5-tricarboxy cyclopentyl acetic dianhydride (TCDA) and DADE, abbreviated TCDA-DADE, to hydrogen and nitrogen are between those of BPDA-DADE, Kapton[®] and BDA-DADE, and it has highest ideal separation factor for H₂/N₂ or H₂/CO in this series, as shown in Table 2. The effect of upstream pressure on the carbon dioxide permeability of BPTA-DADE and TCDA-DADE, SNDC-DADE composed of sulfonyl norbornane tetracarboxylic-dianhydride and DADE, is shown in Fig.10. BPDA-DADE showed no effect on upstream pressure and the transport property was simply expressed by the dual mode transport model, because of the strong intersegmental forces. The effect of upstream pressure differs with chemical structure for the polyimides with rather than the soft backbone structure. These phenomena influence the permselectivity. Gas permeability, diffusivity and the separation factor of Upilex[®] are shown in Figs.11,12 and 13, respectively.

Recently, Mitsubishi Chemical Co. has requested Japanese Patent Application Laid-open for various kinds of new polyimides. The chemical components of these polyimides and their gas transport properties are summarized in Tables 3,4 [12]. The effect of thermal treatment[13] and the fluorination of polyimide membranes [13], 6FDA-MTMB, and 6FDA, PMDA-MTMB, are also summarized in Tables 5 and 6.

The thermal treatment of these polyimide membranes at 300°C for 1 hr gave a remarkable increases in both permeability and the ideal separation factors for H₂/CH₄ and CO₂/CH₄. The thermal treatment at a higher temperature, 400°C, increased the selectivity but decreased the permeability. The fluorination of the polyimide increased the selectivity, but decreased remarkably gas permeability.

If the permeability coefficients for carbon dioxide are plotted versus the ideal separation factor, CO₂/CH₄, for these polyimides [14], it is easy to understand the excellent transport property of these polyimide membranes. As shown in Fig.14, BPDA-DADE and BPDA-DADE, DADM and BDA-DADE are now being used in industrial separation processes as for gas mixtures or vapor mixtures in Japan, as will be discussed in the following section.

Very recently, Ube Industries has developed highly permeable polyimide membranes composed of BPDA and/or 6FDA as acid components and diamine containing diphenylene sulfone, DADS, and/or xanthene, DAXe, xanthone, DAXo, structures. Their asymmetric hollow fibers can be easily prepared by the identical

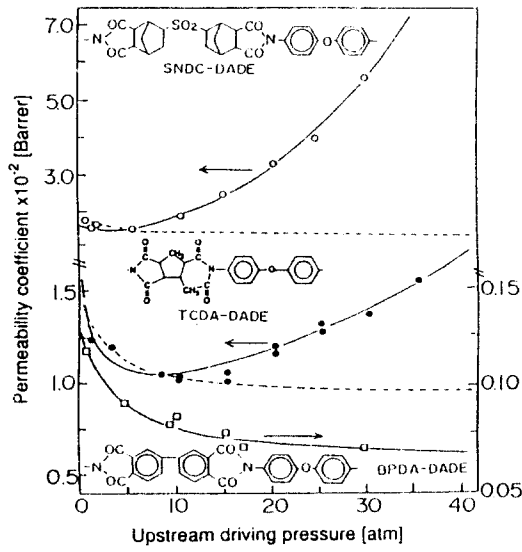


FIGURE 10. Apparent permeability coefficients as a function of supplied pressure for carbon dioxide: (O) SNDC-DADE; (●) TCDA-DADE; (□) BPDA-DADE.

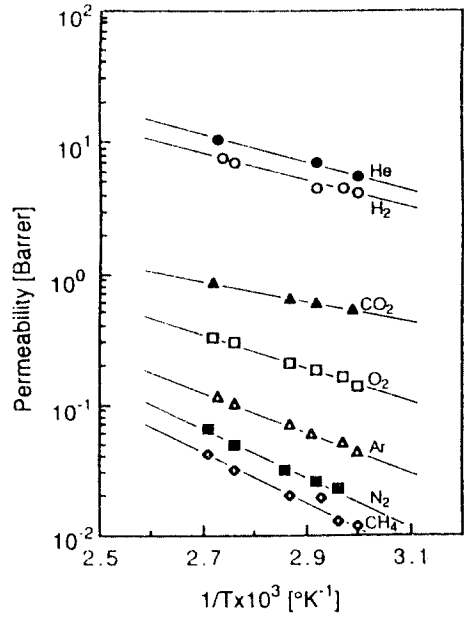


FIGURE 11. Effect of temperature on the gas permeability of Upilex®.

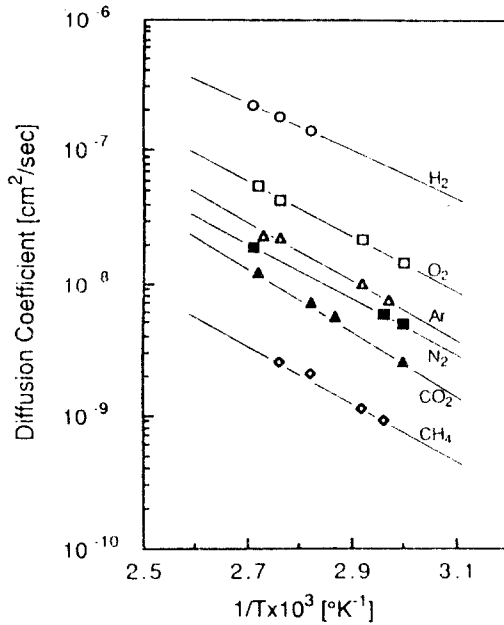


FIGURE 12. Effect of temperature on the gas diffusivity of Upilex®.

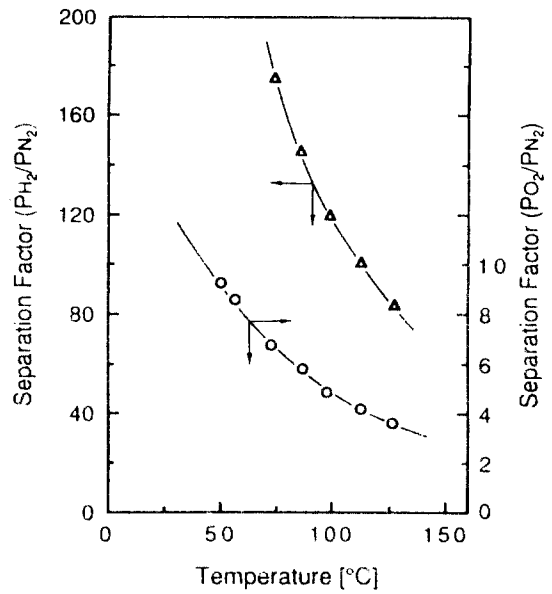


FIGURE 13. Effect of temperature on the gas solubility of Upilex®.

TABLE 3
Gas Permeability of Various New Polyimide Membranes

| Composition of polyimide (millimoles) | | | | | | Gas permeability <i>P</i> (barrers) | | | | | | |
|---------------------------------------|------|------|------|---------|------|-------------------------------------|----------------|-----------------|----------------|-------------------------------------|--------------------------------------|------------------------------------|
| Carboxylic dianhydride | | | | Diamine | | °C | H ₂ | CO ₂ | O ₂ | H ₂ / CH ₄ | CO ₂ / CH ₄ | O ₂ / N ₂ |
| BPDA | DSDA | BTDA | PMDA | TMBD | DADE | | | | | | | |
| 21 | — | — | — | 21 | — | 30 | 46.9 | 19.8 | 5.09 | 77 | 32 | 6.0 |
| | | | | | | 100 | 96.0 | 25.8 | 11.30 | 44 | 12 | 4.0 |
| — | 21 | — | — | 21 | — | 30 | 55.2 | 22.9 | 7.80 | 75 | 31 | 4.9 |
| — | — | 21 | — | 21 | — | 30 | 63.3 | 33.4 | 10.30 | 49 | 26 | 4.0 |
| — | — | — | 21 | 21 | — | 30 | 59.6 | 35.3 | 11.20 | 54 | 34 | 3.7 |
| 26.25 | — | — | — | 21 | 5.25 | 30 | 40.8 | 16.0 | — | 87 | 34 | 5.8 |
| — | — | — | 26.5 | 21 | 5.25 | 30 | 53.2 | 24.4 | — | 72 | 33 | 4.9 |

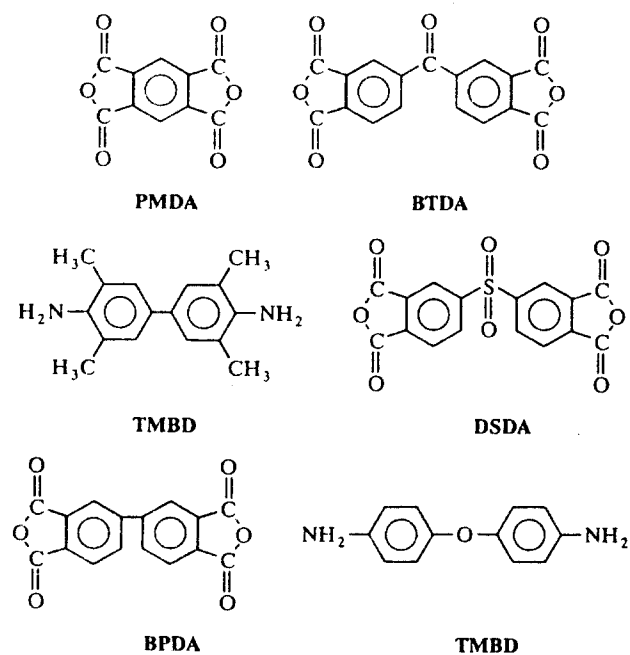


TABLE 5
Effect of Thermal Treatment on Gas Permeability of 6FDA-Polyimide Membranes

| Gas | Gas permeability <i>P</i> (30°C) (barrers) | | | | | |
|----------------------------------|--|------------|------------|------------|------------------|------------|
| | Room temp. | 6 FDA-MTMB | | | 6FDA,PMDA ~ MTMB | |
| | | 300°C, 1 h | 350°C, 1 h | 400°C, 1 h | Room temp. | 300°C, 1 h |
| H ₂ | 73.5 | 222 | 200 | 212 | 150 | 355 |
| CO ₂ | 68.2 | 223 | 175 | 141 | 103 | 394 |
| CH ₄ | 2.62 | 8.6 | 5.98 | 3.03 | 3.47 | 17.5 |
| H ₂ /CH ₄ | 28 | 26 | 34 | 70 | 43 | 20 |
| CO ₂ /CH ₄ | 26 | 26 | 30 | 47 | 30 | 23 |

TABLE 6
Effect of Fluorination on Gas Permeability
of 6FDA-Polyimide Membranes^a

| Gas | Gas permeability <i>P</i> (30°C) (barrers) | | |
|----------------------------------|--|--|--|
| | Before fluorination | F ₂ / N ₂ (4 vol%) | F ₂ / N ₂ (4 vol%) |
| H ₂ | 300 | 99.8 ^b | 112 ^c |
| CO ₂ | 277 | 13.3 | 26 |
| CH ₄ | 11 | 0.16 | 0.372 |
| H ₂ /CH ₄ | 27 | 616 | 301 |
| CO ₂ /CH ₄ | 27 | 82 | 70 |

^a Fluorination for 1 hour at room temperature.

^b 4.23 wt% fluorine.

^c 8.43 wt% fluorine.

TABLE 7
Some Properties of Fluorine-Containing Copolymer Membranes
and Their Oxygen Permeability

| Copolymers | Polymer composition (mol ratio) | Morphology | Solubility at acetone THF | Specific gravity at 20°C (g / cm ³) | <i>T_g</i> ^a (°C) | Oxygen permeability | | Tensile properties | |
|-------------------------|---------------------------------|---------------------|---------------------------|---|--|--|--|---|---------------------|
| | | | | | | <i>P</i> _{O₂} (barrer) | α (<i>P</i> _{O₂} / <i>P</i> _{N₂}) | TB ^b (kg / cm ²) | EB ^c (%) |
| CTFE/VAc | 39/61 | Amorphous | ○ | — | — | 0.54 | 3.8 | — | — |
| CTFE/Vt-Bu · Bz | — | Amorphous | ○ | — | — | 7.8 | 4.7 | — | — |
| CTFE/VPv | 40/60 | Amorphous | ○ | 1.244 | 85 | 10.3 | 4.8 | 418 | 8 |
| TFE/VPv | — | Amorphous | ○ | 1.224 | 84 | 10.4 | 4.2 | 401 | 13 |
| CTFE/ <i>i</i> -BVE/VAc | 49/39/12 | Amorphous | ○ | — | 25 | 7.2 | 4.8 | 241 | 274 |
| CTFE/ <i>i</i> -BVE/VPv | 52/41/7 | Amorphous | ○ | — | 33 | 7.2 | 4.8 | 292 | 15 |
| CTFE/ <i>n</i> -BVE/VPv | — | Amorphous (elastic) | ○ | — | — | 7.0 | 2.9 | 33 | 650 |

^a Glass transition temperature.

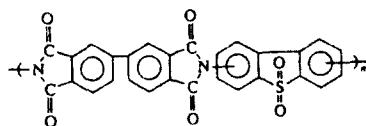
^b Tensile strength.

^c Tensile elongation.

TABLE 8
Size of Module and Unit, Oxygen Enrichment Membrane Type

| | EYO-MU-20 | EYO-MK-20 | EYO-MK-50 | EYO-MK-100 |
|----------------------------------|-----------------|------------------|------------------|-------------------|
| Size of membrane (mm) | 17 × 386 × 326 | 17 × 1140 × 326 | 17 × 1140 × 326 | 17 × 1140 × 326 |
| Number of sheets | 20 | 20 | 50 | 100 |
| Size of unit (mm) | 390 × 600 × 370 | 385 × 1690 × 410 | 895 × 1690 × 455 | 1790 × 1690 × 455 |
| Weight of unit (kg) | 20 | 50 | 110 | 210 |
| Flux (m ³ /h at 20°C) | 3 | 10 | 25 | 50 |
| Conc. of O ₂ at 20°C | | | 30 | |
| Reduced pressure (mmHg) | | | — 560 | |
| Available temperature | | | — 10 ~ +40°C | |

method for BPDA-DADE asymmetric fibers. The one example of oxygen permeation rate and the separation factor for O_2/N_2 at room temperature is $1.01 \times 10^{-9} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ and 4.7, respectively[15]. The hollow fibers are now being used for nitrogen enriched air.



BPDA-DADS

D. Fluorine containing polymer membranes

Asahi Glass Co., Ltd. investigated new polymer membranes containing fluorine. Tetrafluoroethylene, TFE, and/or monochlorotrifluoroethylene, CTFE, were used for copolymers which include are copoly(TFE-PMD), copoly(TFE-*i*-BuVE), copoly(CTFE-*n*-BuVE), copoly(TFE-VPv), and copoly(CTFE-VPv), etc., (PMD: perfluoro(2-methylene-4-methyl-1,3-dioxolane), (*i*-BuVE: iso-butyl vinyl-ether, *n*-BuVE: *n*-butyl vinyl ether, VPv: vinylpivalate). These fluoro-copolymers have advantageous and disadvantages depending on the comonomers. The permeability coefficient of poly(PMD) to oxygen at 20°C is 40 Barrer and the ideal separation factor for O_2/N_2 is 4.2, but the polymer does not dissolve in any solvent except the perfluoro-solvent and the permeability of copoly(TFE-PMD) was less by one order of magnitude than poly(PMD)[16]. Copolymers containing alkyl vinyl ethers dissolve in common solvents and are rubbery, which mean low separation factors. Although the permeability coefficient of oxygen is, of course, higher than that of polytetrafluoroethylene, PTFE, it is of the order of one Barrer [17].

On the other hand, fluoro-copolymers containing VPv showed the permeability coefficient of oxygen of the order of 10 Barrer and the ideal separation is more than 4, as summarized in Table 7 [18]. It is possible to prepare ultrathin membranes from these copolymers by method of spreading on surface of water. These copolymer membranes are used for producing oxygen enriched air as will be shown in the following section.

E. Composite membranes of siloxane containing polyurethanes

Mitsubishi Rayon Co. Ltd. has developed a novel multi-layered composite hollow fiber membrane, MHF, with an ultrathin dense layer inserted between layers and has superior properties for use as an artificial lung [19]. The structure of MHF is shown in Fig.15.

MHF is composed of two porous layers consisting of poly(4-methyl pentene-1) and an ultrathin dense layer consisting of silicone-containing polyurethane. MHF was prepared by a melt-spinning and stretching method. The dense membrane could also be prepared by a solvent casting method from a solution of polyurethane in chloroform whose membrane thickness was $120 \mu \text{ m}$. The effect of temperature on the oxygen permeation rate for the dense membrane and the MHF is shown in Fig.16. The permeation rate of the MHF was extremely high, $1 \times 10^{-4} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ at room temperature. The thickness of the ultrathin dense layer estimated from the gas permeation rate was approximately $0.5 \mu \text{ m}$. The activation energies for oxygen and nitrogen permeation for the dense ultrathin membrane were 19.0 and 20.8 kJ/mol, respectively, which were almost equal to those of MHF from

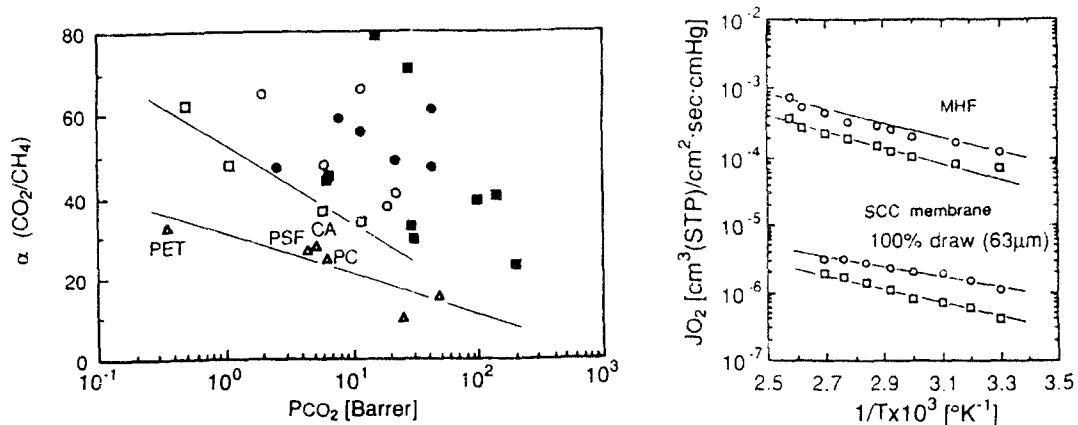


FIGURE 14. Dependence of ideal separation factor α on permeability coefficient for CO_2 in polyimides at 35°C : (○) PMDA-polyimide; (●) 6FDA-polyimide; (■) polyimides developed by Mitsubishi Chemical Co. Ltd.

FIGURE 16. Permeation rate of oxygen and nitrogen of three-layered composite membrane. The multilayered composite membrane is abbreviated MHF. The SCC membrane is a single siloxane-containing polyurethane dense film. The slopes of these Arrhenius plots are almost the same. This suggests that there is no pinhole in ultrathin siloxane-containing polyurethane in the center of MHF.

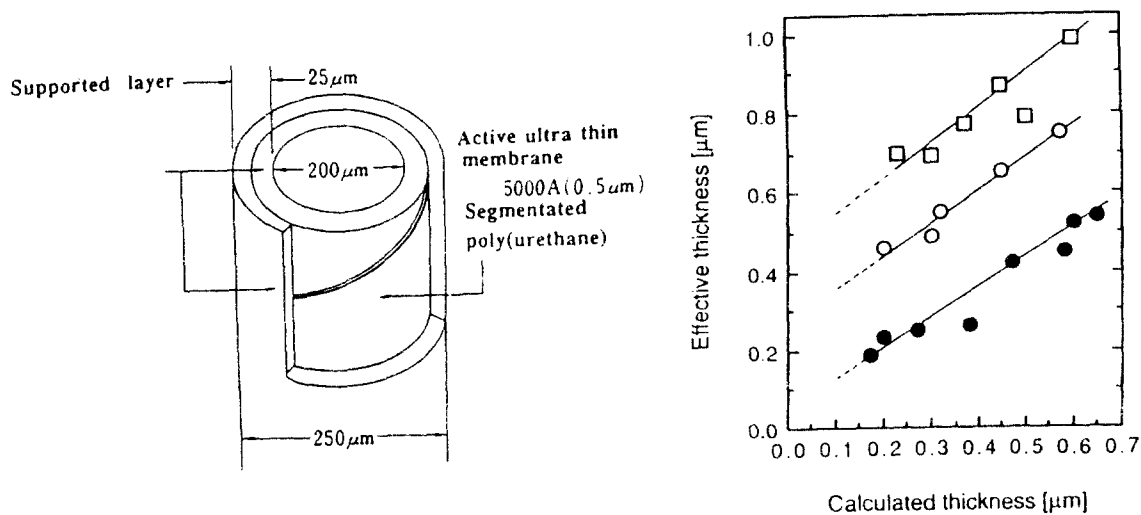


FIGURE 15. Model of structure of three-layered hollow fiber.

FIGURE 17. Calculated thickness vs. effective thickness: Thicknesses of the membranes prepared by the water surface spread process method were calculated from the weight, density of the polymer, and the area. Effective thickness means the minimum thickness obtained for which the gas permeability coefficient and flux of the composite membrane are coincident.

Fig.13. This suggest that the gas transport property of the ultrathin layer is identical with that of the dense membrane. Although the pore structure effect such as porosity and pore size was found to be significant, the resistance of the porous layers was ignored in the porosity range above 40 %.

III. INDUSTRIAL APPLICATIONS OF MEMBRANES FOR GAS SEPARATIONS IN JAPAN

In the previous section, polymer membranes developed in Japan for practical use in industrial applications along with their fundamental gas transport properties described. In this section, the industrial applications of these membranes are described. Materials for practical use in gas separation requires at least three attributes, viz. excellent permeation characteristics - productivity, selectivity - , processability for ultrathin and durability.

A. Oxygen enrichment application

In 1970, the Japanese economy encountered the so-called "OIL SHOCK", an abrupt increase of petroleum prices. Oil, of course, is the most important energy source in Japan and is almost 100 % depending on imports. There are relatively large amounts of coal in Japan called "PEAT", however the quality is not good. Generally, this peat is very difficult to burn by air. The Japanese government decided on an energy policy that included research for producing oxygen enriched air by membranes. If oxygen enriched air is used, then the efficiency for combustion should be increased. Although there are competitive technologies such as absorption processes and a low-temperature processing, membrane process would be more economical in some conditions. The other important application of membranes for their separation is medical use.

1. Oxygen enrichment for combustion and for medical use by polymeric membranes

In the application of polymeric membranes for oxygen enrichment in combustion, a large volume of oxygen enriched air, but not necessarily pure oxygen, is required. Therefore, Matsushita Electric Co. developed the polydimethylsiloxane-polyvinylphenol block copolymer, HS-polymer, membrane and the composite poly[1-(trimethylsilyl)-1-propyne], PMSP, membrane which were explained in detail in the previous section.

HS polymer membranes as thin as 300 to 600 A were prepared by Langmuir-Blodgett process, that is the water surface spread process, followed by laminating on porous polypropylene sheet, Duragard 2400. Ultrathin membrane, e.g. 100 A, are possible.

The limiting thickness depends on the pore diameter of the supporting porous sheet that will avoid rupture of the thin membrane. Fig.17 shows the relationship between the calculated thickness of PMSP membranes obtained by the water surface spread process and the effective thickness obtained by the permeation experiment. The relationship between the effective thickness and the ratio of oxygen and nitrogen fluxes is shown in Fig.18 [1]. From Fig.17, the effective thickness is coincident with calculated thickness for the block copolymer whose siloxane content is 70 %, and the effective thickness increases with increase in the siloxane content. If the effective thickness is less than a limiting value, the separation factor drastically decreases. This suggests there are some defects in the membrane. If a separation factor 2 is to be reached, the effective thickness must be increased more the higher the siloxane content is, as shown in Fig.18. For a combustion system, about 28 ~ 30 % oxygen enriched air is enough. This type of membrane was employed for a combustion system for the first time by Matsushita Electric Co. Ltd. in 1981. The size of module and the unit of oxygen enrichment membrane type are summarized in Table 8.

Asahi Glass Co.Ltd. developed two types of fluorine containing polymeric membranes with the trade name is HISEP: for a large scale application and for medical use.

For medical use, membranes which can produce 40 % oxygen enriched air are required for patients with diseases of the respiratory organs. The ideal separation factor, P_{O_2}/P_{N_2} of 2.7 is required to obtain 40 % oxygen enriched air. However, in the case of the ideal separation factor, the partial pressure on the permeated side is nearly zero. This is not practical. Therefore, an ideal separation factor that is greater than 4 is the minimum requirement. At the same time, a flux of about 4 to 8 ℓ /min is also required. It is quite reasonable to choose poly(4-methyl pentene-1), PMP. Teijin Co.Ltd. developed such an apparatus using ultrathin PMP membrane.

2. The combustion system using oxygen enrichment membranes

The basic flow sheet of the HISEP gas separation system developed by Asahi Glass Co.Ltd is shown in Fig.19. This is a medium size of apparatus with a membrane area of 7.8 m^2 . The large scale apparatus is also available. Permeate gas existing at the low pressure side of the membrane module is removed by a vacuum pump. Membrane modules and complete sets varying in size and also for testing to meet a variety of application requirements are offered. Therefore, the most suitable module or set can be chosen to meet needs. As can be seen in Fig.19, the system is extremely simple and has only two or three moving parts, which ensure reliability.

3. The application to the medical use

a. The permeation rate 4 ~ 8 ℓ /min of oxygen enriched air of which oxygen concentration is 40 % is required. This value is not so difficult attain and the membrane modules are generally of the plate and frame type. In the case of HISEP, the module is as follows: dimension [mm]: 280 x 600 x 83; area of membrane [m^2]: 2.8; pressure of feed gas [atm]: 1 ; pressure of permeate [atm]: 0.2 ~ 0.3.

b. One of the special applications of the gas permeable membranes for medical use is an artificial lung. A multilayered composite hollow fiber, MHF, was prepared by using Mitsubishi

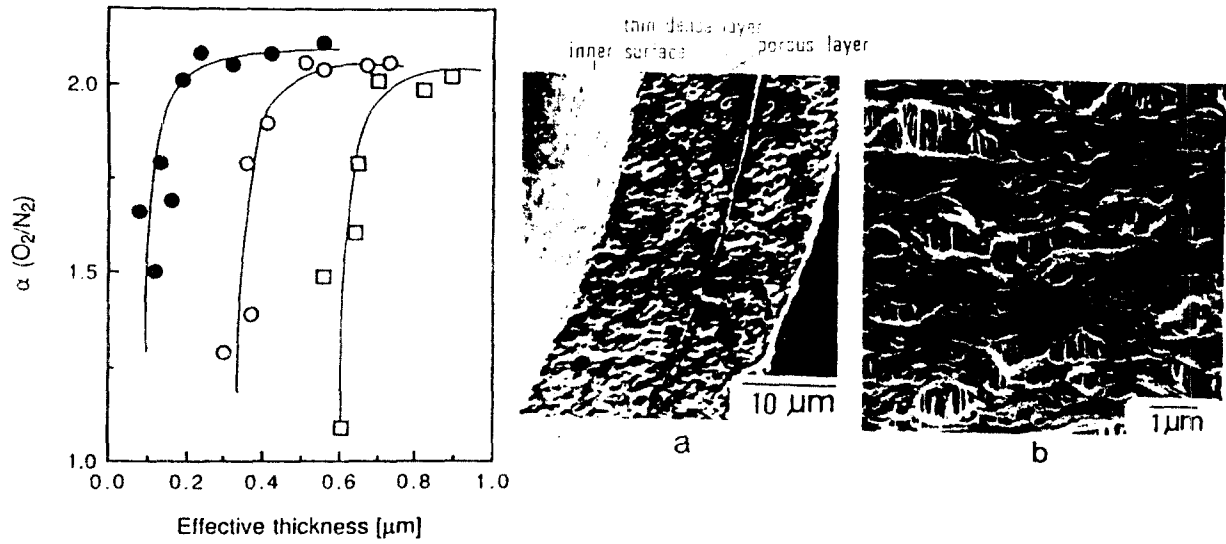


FIGURE 18. Selectivity vs. effective thickness: The thicker membranes were required to keep the inherent separation factor of HS-polymer, in which siloxane content is high.

FIGURE 20. Photographs of the three-layered hollow fiber composed of porous polyolefin films and the siloxane-containing polyurethane ultrathin membrane for medical use: (a) horizontal cross section; (b) inner surface.

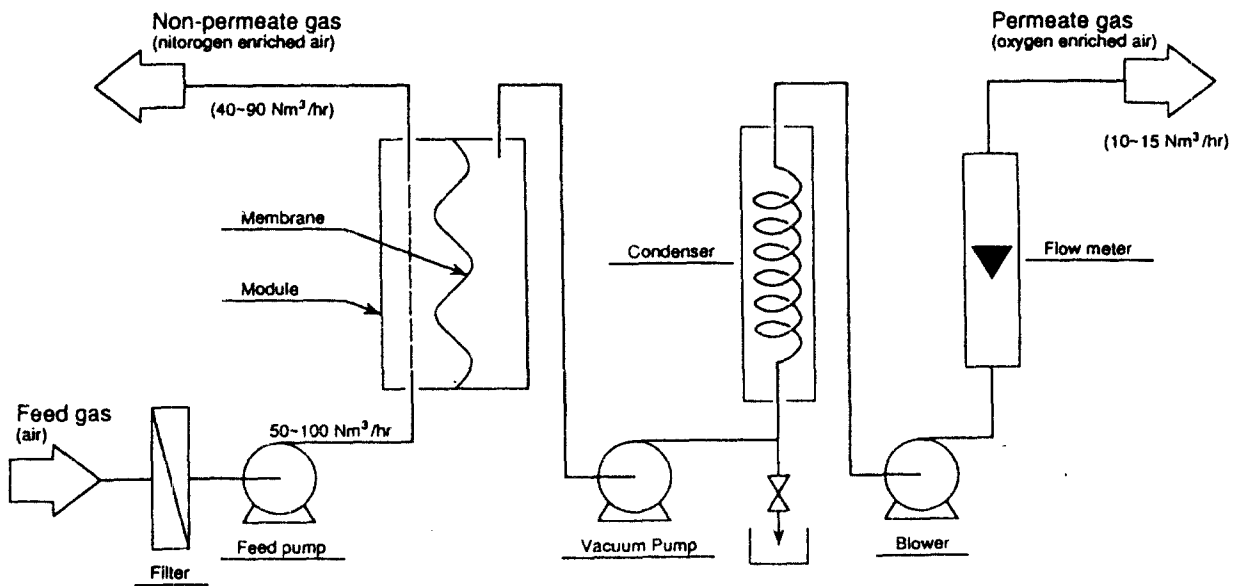


FIGURE 19. The oxygen enrichment flow sheet.

Rayon Co, Ltd, the melt spinning and stretching method. The name of "MHF" means the multilayered composite hollow fiber by this company and MHF being used is a three layered one. Fig.20 shows photographs of the hollow fiber membrane, horizontal cross section and inner surface [20]. The ultrathin middle layer which is made of thermoplastic siloxane containing segmented polyurethane, performs the gas permeation. Both of the microporous layers which are made of polyethylene provide mechanical strength and protection of the ultrathin middle layer. The oxygen transfer rates, the carbon dioxide removal rates, and their change after a period of time were evaluated with MHF using heparinized bovine blood (Hct=34 %, Hb=12 g/dl, SvO₂= 65 + 3%). Blood flow rates were adjusted to 1.0 l /m² · min and oxygen gas flow rates were adjusted to the value of the blood flow rates. In this condition, the effect of the oxygen permeation rate [cm³ (STP)/cm² · sec · cmHg] in a gas/membrane/gas system on the oxygen transfer in a gas/membrane/liquid system is shown in Fig.21. The MHF showed long term stability of gas transfer performances and no serum leakage making it quite suitable for use as an artificial lung.

B. Nitrogen enrichment application

1. Nitrogen enrichment performance

Oxygen enriched air and nitrogen enriched air are of contrast. The latter is in the unpermeated side. Nitrogen enriched air is useful for small scale chemical experiments and for the prevention of explosions or of oxidation in the semiconductor industries and food packaging industries in a large scale. Ube Industries, Ltd. has developed "UBE N₂ SEPARATOR" for both scales. The membrane is a new asymmetrical polyimide hollow fiber as described in the previous section. Nitrogen percent and fluxes for one module in the case of 7 kg/cm² supplied pressure at 25°C are 99%-0.34 Nm³/hr and 95%-1.0 Nm³/hr in small scale equipment and 99%-23 Nm³/hr, 95%-70 Nm³/hr in a large scale equipment, respectively, as one of the examples. The size of the module, L x D x d [mm] is (630~1551) x (65~343) x (43 ~ 216).

2. Process flow scheme

The process flow scheme for a large scale equipment is shown in Fig.22. As the membrane is a polyimide, the apparatus has a heating unit installed especially for a large scale use to avoid damage to the module by humidity. There are very small amounts of various gases in nitrogen. They are oxygen, argon, carbon dioxide and water vapor. However, the concentration of argon and carbon dioxide is about 1 % and less than 10 ~ 30 ppm, respectively, and the dew point of water vapor is less than minus 40°C. The compressed air is supplied to the inner side of the hollow fibers.

C. Hydrogen separation from the mixture of hydrocarbons in petroleum industries

Originally membranes, which were designated for hydrogen separation, developed for the separation of hydrogen/carbon monoxide. The mixture of hydrogen and carbon monoxide is called "synthetic gas" and is used for synthesizing various kinds of organic chemicals at the elevated temperature. To remove unreacted hydrogen, a high separation factor such as 80 and a high permeation rate 10⁻⁴ cm³/cm² · sec · cmHg at above 100 °C are required.

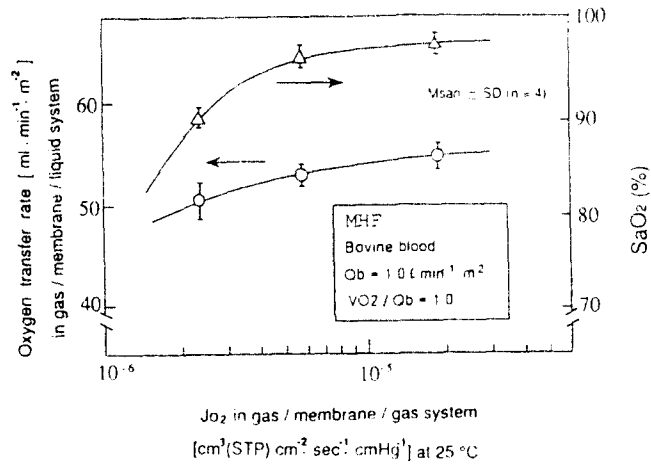


FIGURE 21. Oxygen transfer performances of gas-membrane-liquid system vs. the oxygen flux in the gas-membrane-gas system, using MHF: SaO₂ is the percentage of oxygen vs. the saturation of oxygen in the oxygenated blood.

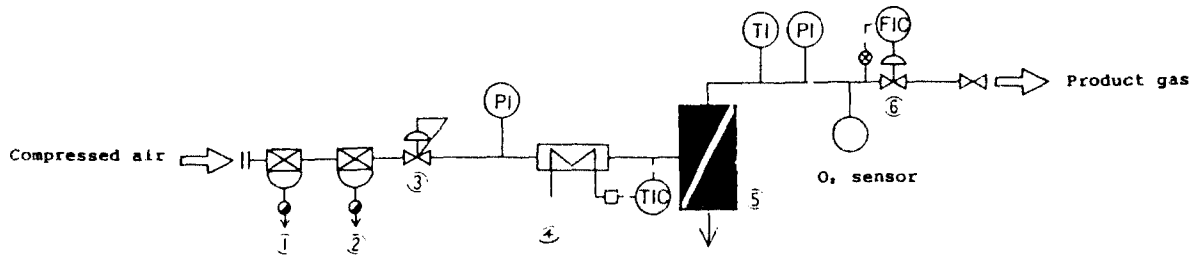


FIGURE 22. Process flow scheme for large-scale nitrogen enrichment equipment: ① air filter; ② mist separator; ③ regulator; ④ electric heater; ⑤ membrane module; ⑥ flow control valve.

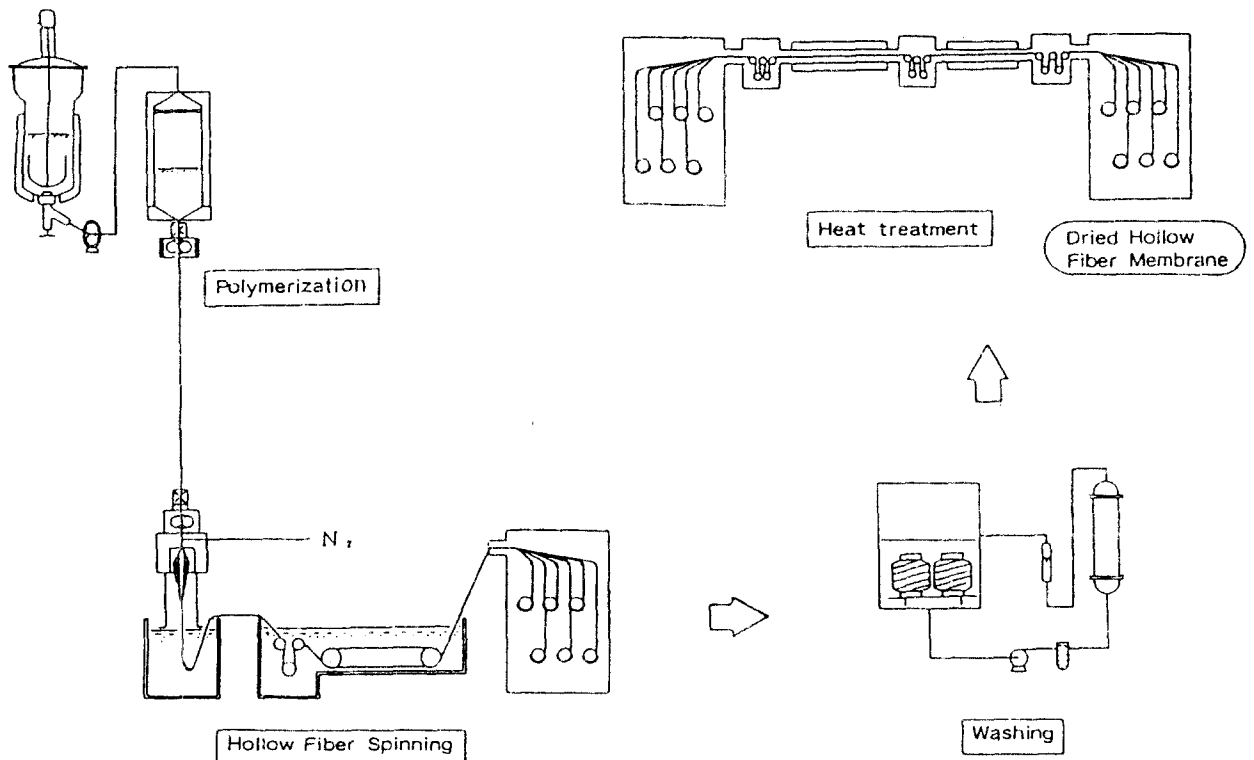


FIGURE 23. Manufacturing process of polyimide hollow fiber.

The membrane used for separation of hydrogen from the mixtures of carbon monoxide is a new type of polyimide based on biphenyl tetracarboxylic dianhydride, BPDA, and diamino diphenyl ether, DADE, trade name "Upilex" developed by Ube industries. one of the typical gas transport properties was shown in the previous section.

1. Membrane module

For the practical use of the polyimide membranes for gas separation the most important points are producing the ultrathin active skin layer on the surface of hollow fibers and casting hollow fibers with enough strength and flexibility for manufacturing modules. BPDA-DADE, BPDA-DADE, DAM (diamino diphenyl methane) are not soluble in most organic solvents including DMAC (dimethylacetamide), but they are soluble in p-chlorophenol. The production process for making polyimide hollow fiber is shown in Fig.23. Polymerization was carried out in p-chlorophenole as a solvent, and the dope is fed to the spinning nozzle, then the fiber is led to the aqueous ethanol coagulant. The wound fiber is washed in organic solvent and then treated in a high temperature oven. In this process, the active thin layer is inevitably on the outside of the hollow fiber. Also, the production process of a double layer asymmetric hollow fiber has been developed, in which two different polyimide dopes are extruded simultaneously from a cycle nozzle with double slits, as shown in Fig. 24. The polymer of the inner layer forms the porous wall of the supporting layer and the outer layer is an ultrathin skin for gas separation. By using this type of hollow fibers, in some cases the permeability was increased five times more than single layer membranes. The double layer membrane has already been used for hydrogen separation processes on a commercial basis.

It has become clear that polar groups, such as $-S-$, $-SO_2-$, etc. introduced in polyimide and long aliphatic chain structure in diamines increases diffusivity. It is not always possible to cast an asymmetric hollow fiber of high performance. In such a case, the hollow fiber can be cast using copolyimides with good solubility in a particular solvent, excellent spinnability and the excellent processability. Copolyimides change the molecular structure and the coagulation rate of the dope to produce a membrane structure with sufficient strength and high performance.

Fig.25 shows the permeation rate of typical BPDA based polyimide membranes for various gases and vapors. These are available in commercial basis. Type B-H is used for hydrogen separation, Type C is used for dehumidification and Type D for the dehydration of alcohols and some organic solvents. The chemical structure of these Type of polymers has not disclosed yet, but Type B-H is seemed to be BPDA-DADE, and Type C and Type D are copolyimides of BPDA-DADE with BPDA-DAM.

2. Process flow scheme

Typical flow schemes for the recovery of hydrogen and the purification of hydrogen in commercial plants are shown in Fig. 26,27, respectively. The conditions such as flow rate, pressure difference and compositions of the mixed gases also shown in these figures. The membrane process shown in Figs.26,27 have been used for the recovery of hydrogen from platformer off gas in petroleum industries. The BPDA-DADE polyimide hollow fiber is used, because of its excellent chemical resistance

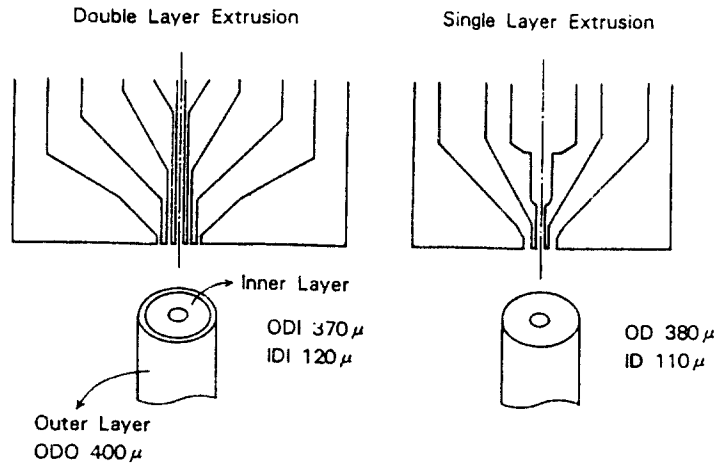


FIGURE 24. Preparation of double-layer asymmetric hollow-fiber membrane.

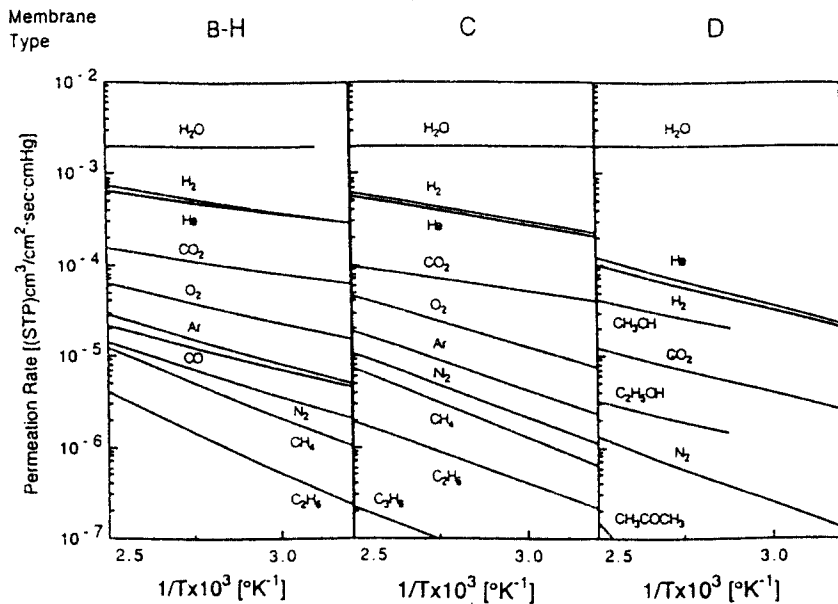


FIGURE 25. Gas permeation rate of typical BPDA-based polyimide membrane, Upilex®: Type B-H is BPDA-DADE; Types C and D are copolyimides of BPDA-DADE and DAM.

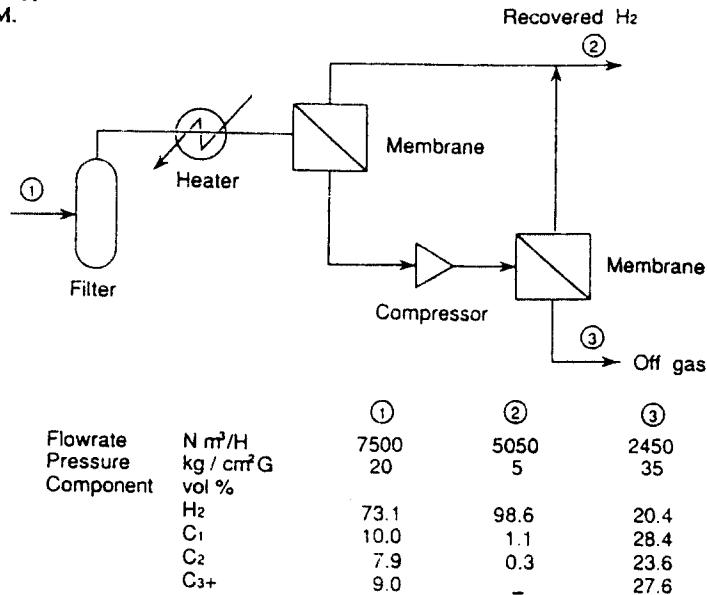


FIGURE 26. Flow scheme for hydrogen recovery in commercial plants.

characteristics for severe conditions, i.e. 27 vol % of hydrocarbon vapors. As has already mentioned in the previous section, the separation factor of H_2/CO or H_2/N_2 is very high, i.e. about 180 at 70 °C, though permeability coefficients are very small.

E. Removing of gases dissolved in water for steamer and ultra pure water

Dainippon Ink Chemical Company (DIC) was successfully able to prepare poly(4-methyl pentene-1) asymmetric hollow fiber whose inside diameter was about 200 μm including skin layer and porous supporting layer. The permeation rate of the hollow fiber to oxygen under dry condition is $2.0 \times 10^{-5} \text{ cm}^3 \text{ (STP)/cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ at 20 °C and the ideal separation factor for O_2/N_2 is 3.8~4.0 and the pressure limit is 4.0 kg/cm². This type of hollow fiber is used in a nitrogen enrichment from air in the USA, but DIC has developed a new apparatus with the Miura Kogyo Company using the hollow fibers for removing the oxygen and the other gases dissolved in water which is used for a steam generating boiler. Fig.28 shows the relationship between water flux and the concentration of oxygen dissolved in water in the retentate under the various reduced pressure at the permeated side at 25°C. The concentration of the oxygen in the supplied water is 8 ppm. The high reduced pressures and the low water flux make for a low concentration of the oxygen in the retentate, such as less than 2 ppm. The degassed water keeps the wall of the boiler clean and thus the life of the boiler is significantly improved.

E. The removal of hydrocarbon vapors and their recovery from air

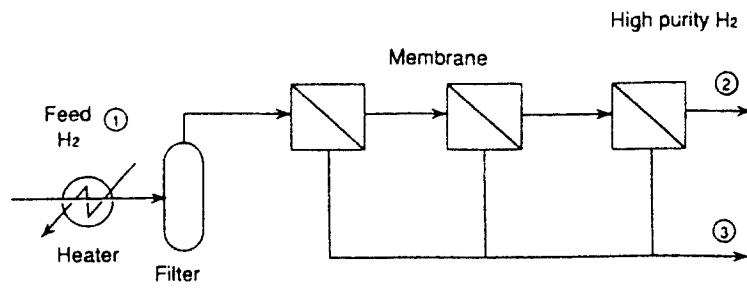
Many industrial processes which use hydrocarbons produce waste air containing hydrocarbons vapor such as gasoline, naphtha, jet-fuel and solvents, etc. In addition to being a loss of valuable petroleum resources, the waste air causes serious pollution problems such as photochemical smog and unpleasant smells, etc.

Recently, Nippon Steel Pipes Co.,Ltd. developed a new type of hydrocarbon vapor recovery system that uses a polyimide membranes with permselectivity for hydrocarbon vapors. The system can be used in refineries, petrochemical plants and petroleum-tank terminals.

The membrane used for the hydrocarbon vapor recovery systems is a polyimide membrane which was developed by Nitto Electric Co.,Ltd. The equipment for this process is furnished to meet conditions for hydrocarbon vapor emission control imposed by ordinances and also to assure economical recovery of hydrocarbon vapors. The typical example of the application of a membrane process is for recovering gasoline vapor from a gas mixture in which 15~50 vol% gasoline vapor and air are present, and thus reducing the gasoline vapor content to less than 5 vol% in the air emission.

1. Membrane modules

Nitto Electric's polyimide BDA-DADE was shown in the previous section. The gasoline vapor separating membrane used in this process consists of two layers, as shown in Fig.29, ultrathin permselective layer and a microporous support layer [21]. The ultrathin permselective layer, followed by a thick intermediate transport layer are BDA-DADE polyimide membrane



| | | ① | ② | ③ |
|-----------|------------------------|-------|----------|-------|
| Flowrate | N m ³ /H | 100 | 70 | 30 |
| Pressure | kg / cm ² G | 26 | 3.0 | 2.0 |
| Component | vol % | | | |
| | H ₂ | 99.07 | > 99.999 | 96.84 |
| | CH ₄ | 0.62 | < 1ppm | 2.09 |
| | N ₂ | 0.25 | 1ppm | 0.86 |
| | Ar | 0.06 | 2ppm | 0.21 |
| | CO,CO ₂ | 12ppm | < 1ppm | 40ppm |

FIGURE 27. Flow scheme for purification of hydrogen in commercial plants.

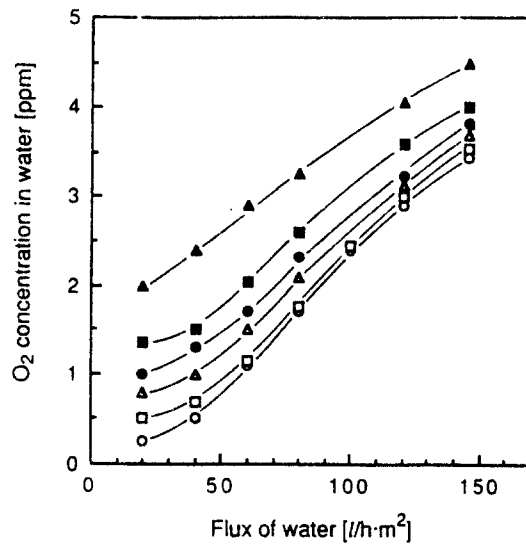


FIGURE 28. Effect of water flux on the concentration of oxygen dissolved in water: degree of reduced pressure (▲) 150 mmHg; (■) 100 mmHg; (●) 80 mmHg; (△) 60 mmHg; (◻) 40 mmHg; (○) 20 mmHg.

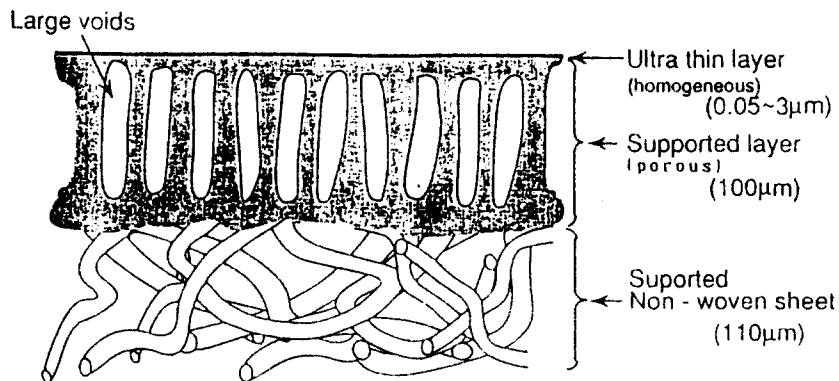


FIGURE 29. Model of structure of aliphatic polyimide composite membrane.

which is a crosslinked, three-dimensional structure, insoluble soluble in hydrocarbon vapors. The BDA-DADE membrane can be used for the recovery of vapors, such as hexane, acetone, methyl ethyl ketone, ethyl acetate, butyl acetate, ethyl alcohol, isopropyl alcohol, toluene, xylene, tri-chloro ethylene, pentane, octane, etc. and for mixtures of air with naphtha and gasoline. As shown in Fig.30, the permeation rate of the BDA-DADE membrane to organic vapors are more than ten times higher than that of N_2 , depending on the kind of vapors. The composite membrane used in this apparatus has vapor permeation rate of $5\sim 20 \text{ Nm}^3/\text{m}^2\cdot\text{hr}\cdot\text{atm}$ which is also more than ten times higher than that of air. Although there are two principal module designs currently in use for an industrial scale, namely, the spiral wound module and the follow fiber module, the former is used in this apparatus.

2. Process flow scheme

A typical flow scheme of the gasoline vapor recovery process using membranes is shown in Fig.31. Gaseous mixture of air with gasoline vapor emitted at a loading terminal has generally very low pressure of the order of ten to a hundred mm H_2O . It is therefore compressed to hundreds of mm H_2O by a blower and then sent to the permeator. The permeate side of the module is kept at a low pressure of $60\sim 100$ Torr by a vacuum pump. The residue (unpermeated) gas is discharged into the air. The residue satisfies the regulated emission of hydrocarbon content, that is less than 5 vol %. The permeated gasoline vapor is sent to a recovery column, where it is absorbed in solvent, a fresh gasoline liquid, and recovered as gasoline product. Typical design conditions for gasoline vapor recovery are summarized in Table 9.

An alternative process for the recovery of gasoline vapor is shown in Fig.32. Gaseous mixture of air with 40 vol.% gasoline vapor is compressed to about 1.5 kg/cm^2 with a compressor and sent to a recovery column, where it is absorbed in fresh gasoline. The tail gas which contains about 20 vol.% of gasoline vapor is then sent to the membrane modules, where the vapor concentration in the residue is reduced to less than 5 vol.%. The gas permeating through the membrane modules is sent back to the feed and recycled.

For gasoline vapor which is composed of multi hydrocarbon components, C_3 through C_7 , the absorption with fresh gasoline liquid is effective. In the case of a hydrocarbon vapor comprised of a single component alone, however, such a porous shown in Fig.33 is effective, which uses a refrigerator instead of the recovery column to condense and recover the vapor concentrated through the membrane.

This membrane process was successfully commercialized in 1987. The membrane process, still in its development stage, is totally superior to another process such as Ambient Temp. & Atmospheric Pressure Absorption, Ambient Temp. & Atmospheric Pressure Absorption and Vacuum Regene, Refrigerated Absorption, Chilling Condensation, and Simple Absorption.

IV. NEW APPLICATION OF MEMBRANES FOR GAS SEPARATION IN THE NEAR FUTURE IN JAPAN

On 27th July 1990, The Research Institute of Innovative Technology for the Earth, RITE, has been established with the aim of tackling the growing threat of global environment

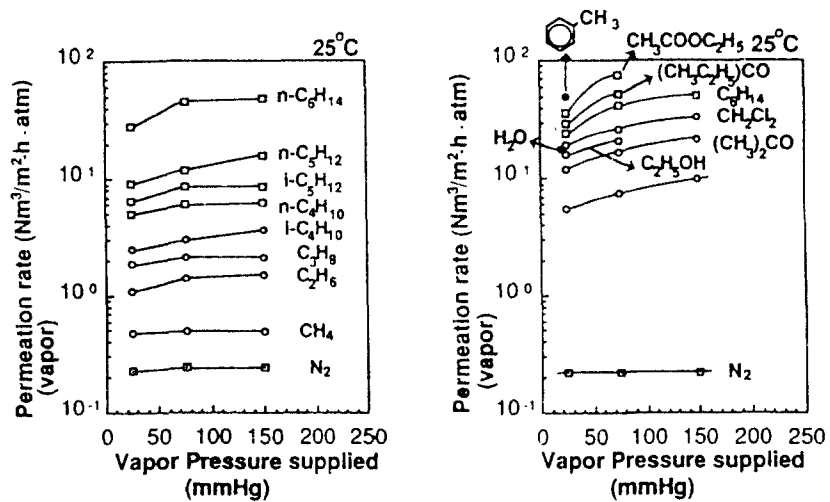


FIGURE 30. Permeation rate of organic vapors for aliphatic polyimide composite membrane.

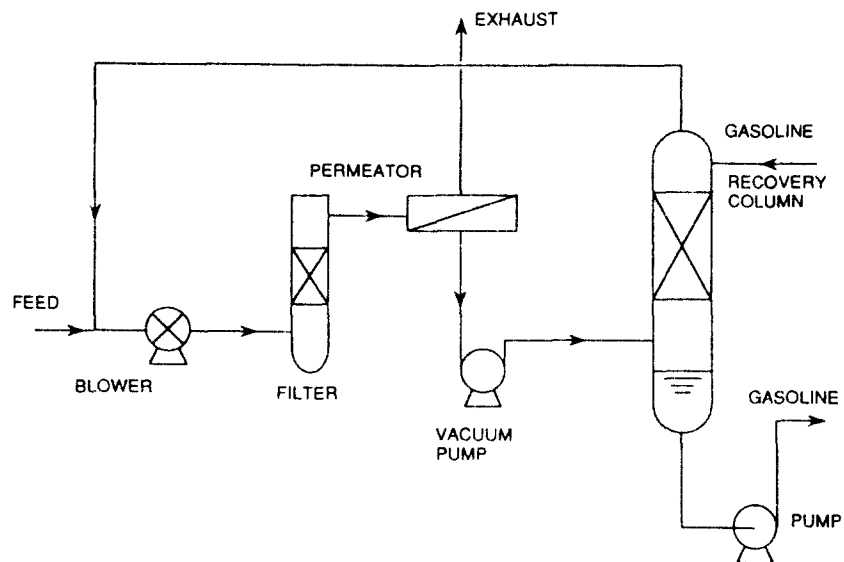


FIGURE 31. Membrane process for gasoline vapor recovery (standard process).

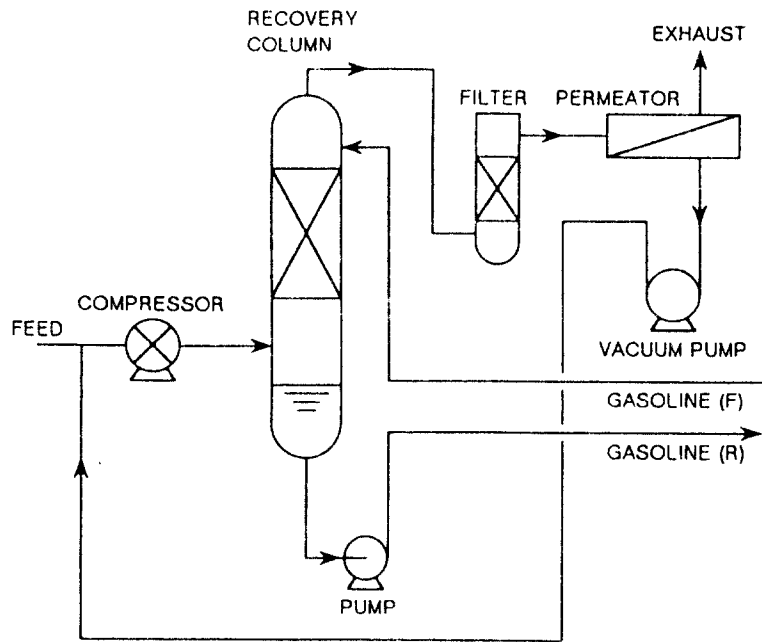


FIGURE 32. Membrane process for gasoline vapor recovery (low-pressurization process).

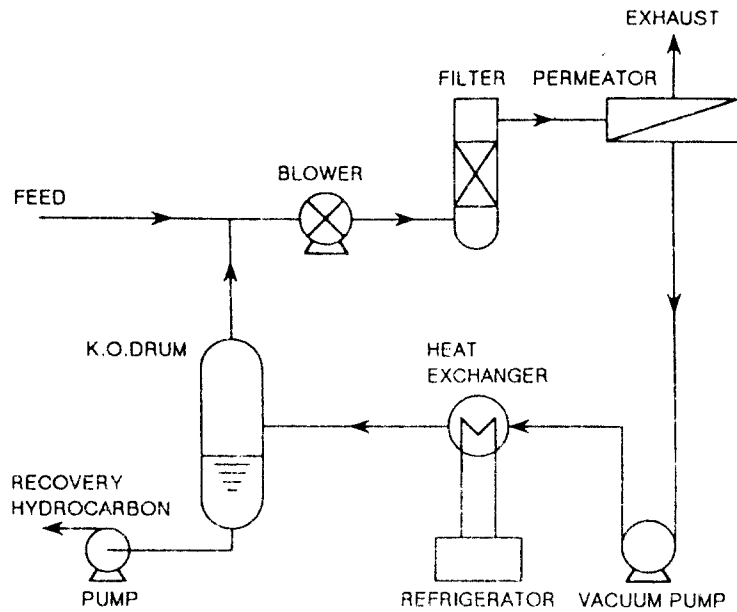


FIGURE 33. Membrane process for organic vapor recovery.

TABLE 9
Condition and Performance of Apparatus
for Recovery of Hydrocarbon Vapors

| | Feed side | | Permeate side |
|-------------|-------------------------|----------------------------|--------------------------|
| Flux | 400 m ³ /day | Conc. of hydrocarbon | 5.0 vol% |
| Pressure | 1 atm | Percentage of removal | 90% |
| Temperature | 35°C | Electric power | About 50 kWh |
| Composition | C ₃ 1.2 vol% | Recovery of hydrocarbon | About 570 liters per day |
| | C ₄ 10.8 | | |
| | C ₅ 17.3 | | |
| | C ₆ 10.3 | | |
| | C ₇ 0.4 | | |
| | Air 60.0 | | |
| | Total 100.0 | | |

problems which rank among the most urgent tasks facing mankind.

RITE has a plan to develop the technology to retrieve carbon dioxide, methane, dinitrogen oxide, etc. which are responsible for the temperature rise or so called Greenhouse Effect. Membranes will be used for solving this problem.

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