Separation of N_2/SF_6 binary mixtures using polyethersulfone (PESf) hollow fiber membrane

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Abstract–PESf hollow fiber membrane was used to recover sulfur hexafluoride (SF_6) from N_2/SF_6 binary mixture gas. To fabricate a hollow fiber membrane, a dry-wet phase inversion method was used. Fiber was post-treated by methanol to increase permeance. Fabricated membrane was characterized by scanning electron microscopy (SEM) and N_2, SF_6 single gas permeation according to temperature and pressure difference. Using N_2/SF_6 binary mixture gas (10 vol% of SF_6), we checked the separation of mixture gas in a manufactured single module according to temperature, pressure difference, and retentate flow rate. The highest SF_6 purity in recovered gas was 50.4 vol% when the pressure difference, temperature, and stage cut was highest in experimental conditions, but the recovery ratio marked the lowest value.

Key words: Polyethersulfone, Sulfur Hexafluoride, Greenhouse Gas, Mixture Gas Separation, Hollow Fiber Membrane

INTRODUCTION

Sulfur hexafluoride (SF_6) is an inert gas used as an insulative material, so it has seen wide application in industries such as the electronics and electric power, as well as in gas insulated switchgears (GIS), gas insulated lines (GIL), and gas circuit breakers (GCB) [1]. However, SF_6 gas has an extremely high global warming potential (23,900 GWP) and remains in a stable state in the atmosphere. Official statistics show that the cumulative SF_6 sales in the world from 1961 through 1999 amounted to 136,172 metric tons [1] and show an increase in SF_6 abundance from near zero in the 1970s to a global mean of 6.7 ppt by the end of 2008 [2,3]. The emissions of SF_6 are targeted for collective reduction under the Kyoto Protocol because of their long atmospheric lifetime (estimated to be between 800 and 3,200 years).

N_2/SF_6 admixtures are receiving attention as a potential substitute for SF_6. Currently, there are two principal recovery methods that have been examined for N_2/SF_6 gas mixtures: pressure swing adsorption (PSA) and membrane separation [4-6].

Membrane technology, especially polymeric membranes, has become an object of attention all over the world because it consumes little power and has good separation ability [4]. Gas separation using a polymeric membrane is fulfilled through a solution-diffusion mechanism [5,7,8]. The mechanism is that gas molecules are dissolved in a high-pressure interface of a membrane, and dissolved molecules are diffused to a low-pressure interface by the segmental mobility of a membrane and get out of the membrane. This mechanism can be divided into two groups: solution into the membrane surface and diffusion in the membrane. The solubility is governed by the affinity between the penetrant and the membrane material. In the diffusion process, the diffusivity depends on the physical properties such as the uprightness of the material and the degree

of crystallization [7]. In the separation of N_2/SF_6 mixtures, N_2 (3.6 Å) and SF_6 (5.02 Å) have different kinetic diameters, so they can be separated by the difference in the diffusion coefficient.

We used Polyethersulfone (PESf) for the fabrication of a hollow fiber membrane because it has good stability, high mechanical strength, high chemical resistance, and high gas permeance in comparison with other membrane materials [5-12]. Furthermore, following post-treatment by methanol, PES can improve to increase permeance and reproducibility [5,8].

Permeance is affected by diffusion coefficients and solubility coefficients, and it can be expressed by the Arrhenius function ($P=P_o e^{-E_P/RT}$). ΔE_P, the activation energy of the gas, is made with ΔE_D (energy of activation for diffusion) and ΔH_S (heat of sorption) [7,12,13]. The activation energy is a distinct character of a gas, so the permeances of two gases are different from one other according to temperature conditions [14], enabling an efficient separation in the mixture gas.

In this study, we checked the relations between the concentration of SF_6 in the retentate side and the recovery ratio according to the temperature, pressure difference, and retentate flow rate.

EXPERIMENTAL

1. Fabrication of Hollow Fiber Membranes

To fabricate hollow fiber membranes, the dry-wet phase inversion method [15-17] was used. The dope solution is a ratable mixture that was composed with PESf (Ultrason® E6020P, BASF, Germany), solvent (N-methylpyrrolidone, NMP, Merck, Germany), and non-solvent (water). It was mixed with a mechanical stirrer (160 rpm, at 80 °C) after PESf removed moisture at 80 °C over a three-day period. To remove bubbles that occurred in the mixing process, the dope solution was left in an vacuum tank for one day. After that, we checked the viscosity with a viscosimeter (LVDV-II PRO, BK instrument, Denmark) at 25 °C.

The dope solution was supplied by using a gear pump, and a 90

micron line-filter was set up for a uniform supply. Internal coagulant (water) was supplied by using an HPLC pump (Series II pump, Lab Alliance, USA). Dope solution and internal coagulant were passed through a double pipe spinneret that had a 0.15/0.9 mm inner/outer diameter. In this study, the air gap - the distance from the spinneret to the first coagulation bath - was fixed at 0.5 cm.

Hollow fiber passed through the first coagulation bath and phase inversion occurred rapidly, moved to the second coagulation bath, was washed out, and coiled around the winder. After this process, fiber was washed in 40 °C running water for six days to remove the remaining solvent. Fiber was post-treated with methanol for two hours to improve flux and was dried in oven at 40 °C, for seven days.

Fiber was characterized by SEM (scanning electron microscopy, S-4700, Hitachi). For this observation, we deposited the fiber in distilled water during two hours and refrigerated it with liquid nitrogen so that it could be maintained with the original cross-section after being cut off. After drying off completely, the membrane was coated with polydimethylsiloxane (PDMS) to remove surface defects and pin-hole. Table 1 is a list of fabrication conditions of the hollow fiber membrane.

Table 1. Fabrication conditions of hollow fiber membrane

Dope compositions	
PESf	27.0 wt%
NMP	68.5 wt%
Water	4.5 wt%
Spinning conditions	
Air gap	0.5 cm
Internal coagulant	Water
Outer coagulant	Tap water
Injection rate of dope solution	3.2 ml/min
Injection rate of internal coagulant	1.0 ml/min
Winding-up speed	11.8 m/min
Coagulation bath temperature	20 °C
Post-treatment	
MeOH	2 hr

2. N$_2$, SF$_6$ Single and Mixture Gas Permeation

At first, we checked single gas permeations through the module under different pressure and temperature conditions. Fig. 1 shows the experimental apparatus with a single module. For the single gas permeation, we blocked the retentate flow rate and supplied 99.999% N$_2$ and 99.98% SF$_6$ (SAFETY GAS, Korea) in the apparatus. P1 in this figure means the pressure difference between the upside and downside of the module.

Permeance can be defined as in Eq. (1):

$$P = \frac{V(STP)}{A \cdot \Delta P \cdot t} \tag{1}$$

P : permeance [GPU] (1×10^{-6} cm^3 (STP)/cm^2·sec·cmHg)
Δp : pressure difference (cmHg)
V : calibrated permeate volume (cm^3)
A : effective area (cm^2)
t : permeate time (sec)

Selectivity can be defined as the permeance ratio between different single gases. That is, selectivity (α_{ij}) between gas i and j can be expressed as in Eq. (2).

$$\alpha_{ij} = P_i / P_j \tag{2}$$

In this study, there were several variables, including temperature, pressure difference, and retentate flow rate, and we wanted to figure out how they affected the membrane to separate binary mixture gas that had 10 vol% SF$_6$ concentration. The oven-controlled tempera-

Table 2. Experimental conditions for mixture gas separation

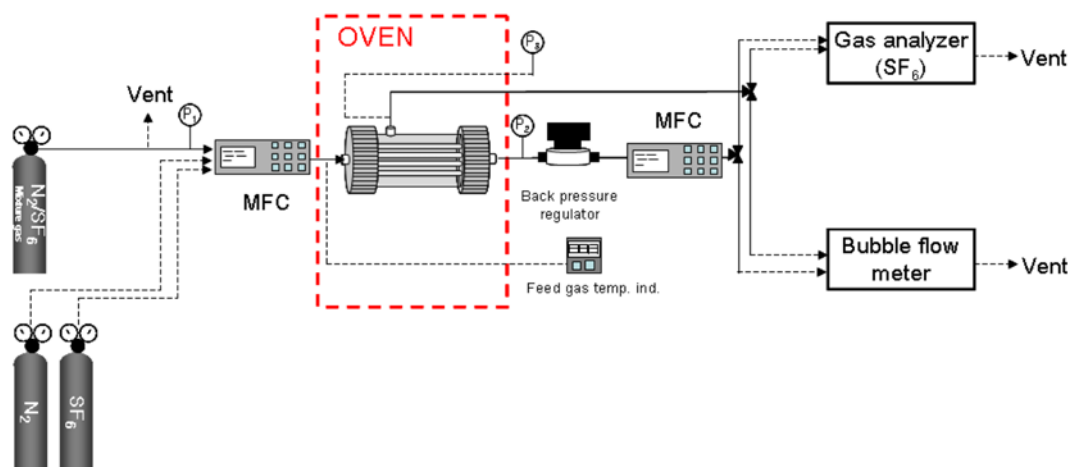| Single gas permeation	
Pressure difference [kg/cm^2]	3/4/5/7/10
Temperature [°C]	25/35/45/65
Mixture gas separation	
Controlled retentate flow rate [cc/min]	150/300/500/1000/1500
Pressure difference [kg/cm^2]	3/5/7/10
Temperature [°C]	25/35/45/65
SF$_6$ concentration in mixture gas	10 vol%

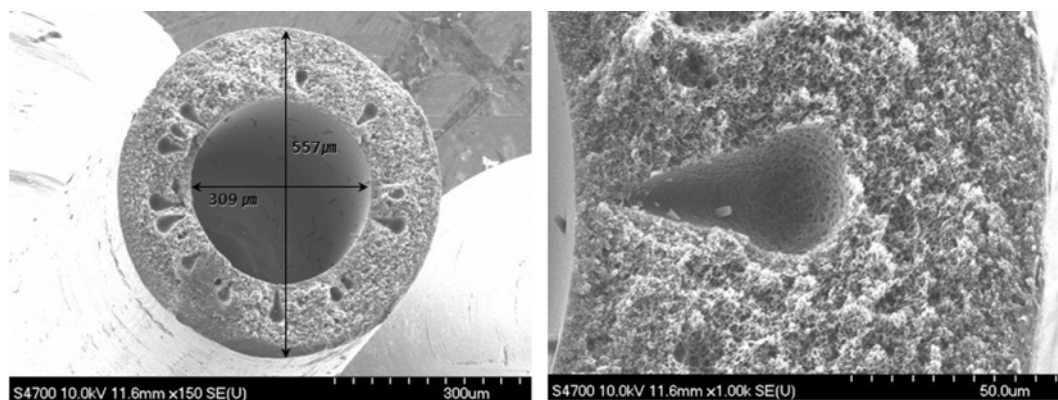**Fig. 1. An experimental apparatus with a single module.**

Fig. 2. SEM photos of fabricated membrane.

ture of the module and operations was measured when the gas temperature was equal to the module temperature. For changing the retentate flow rate at a fixed pressure difference, a back pressure regulator was used. Table 2 shows the experimental conditions for mixture gas separation in this study.

The gas flow rate of the gas permeated was measured by a bubble flow meter, and an SF_6 gas analyzer (SF6-1000, Predicta, USA) measured the concentration of SF_6 in the separated gas. Eq. (3) is a stage cut that can see the permeate flow rate following the retentate flow rate at a fixed temperature and pressure difference.

$$\text{Stage cut } (\theta_P) = \frac{\text{flow rate of permeate side [cc/min]}}{\text{feeding gas flow rate [cc/min]}} \quad (3)$$

SF_6 has a lower permeate speed than N_2, so in comparison with the original mixture gas, there is SF_6 recovery in the retentate side, but loss in the permeate side. The recovery ratio is defined (4) in the experimental condition.

$$\text{Recovery ratio } (\%) = \frac{(\text{flow rate} \times SF_6 \text{ purity}) \text{ in retentate side}}{(\text{flow rate} \times SF_6 \text{ purity}) \text{ in feed side}}$$
(4)

For the accuracy of the test, we checked the mass balance of SF_6, N_2 concentration, and gas flow rate between permeate/retentate side and the feed side. Accuracy rates of over 95% were shown in the results.

RESULTS AND DISCUSSION

1. Fabrication of Hollow Fiber Membranes

The dry-wet phase inversion method was used to fabricate hollow fiber membranes. Dope solution, passed through the spinneret, went through the air gap, where solvent was evaporated. At this time, solvent and dissolved PESf were spread out, so the concentration of PESf increased in the outer side of the fiber. This process formed a close selective layer in this surface of fiber. If the air gap were larger, the selective layer would be thicker because of substantial solvent evaporation. The air gap was 0.5 cm in this study. Post-treatment using organic solvent has a faster solvent exchange speed than using water because organic solvent has lower surface tension. As a result, this process increased the dry speed of the fiber, so the membrane was restrained from forming a selective layer and

had high permeance against the penetrants.

Fig. 2 shows the structural character of the hollow fiber membrane. The cross-section of membrane has an asymmetrical struc-
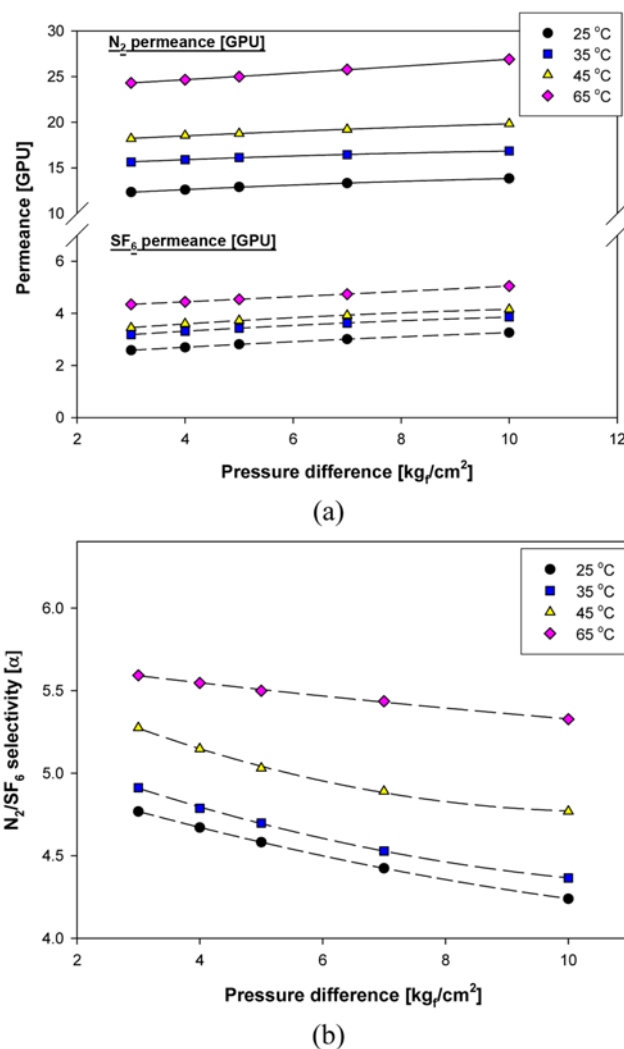

(a)

(b)

Fig. 3. N_2 and SF_6 single gas permeation as functions of pressure difference and temperature: (a) N_2, SF_6 permeance, (b) N_2/SF_6 selectivity.

ture with a close selective layer on the surface and sponge-like structures in the fiber. The membrane has a 557/309 μm outer/inner diameter and a 124 μm thickness. In this research, a module was manufactured that had a 27 cm effective length and a 0.67 m² effective cross-sectional area.

2. N₂, SF₆ Single Gas Permeation

Before separating binary mixture gas, we checked N_2, SF_6 single gas permeations and selectivities of N_2/SF_6 as functions of pressure difference and temperature. Fig. 3 shows the results of their permeance and selectivity.

As a function of pressure difference, permeation had a positive correlation with pressure difference. At 25 °C, when the pressure difference increased from 3 to 10 kg/cm², N_2 permeance increased from 12.3 to 13.8 GPU (12% rate of increase), and SF_6 was from 2.6 to 3.3 GPU (27% rate of increase). Neither of the gases had high growth; however, SF_6's increase was higher than N_2's so N_2/SF_6 selectivity was decreased from 4.8 to 4.2 (13% rate of decrease).

In the function of temperature, permeation had positive correlation with temperature, too. At a 5 kg/cm² pressure difference, when the temperature increased from 25 to 65 °C, N_2 permeance was increased from 12.9 to 25.0 GPU (94% rate of increase), and SF_6 was from 2.8 to 4.5 GPU (61% rate of increase). Therefore, N_2/SF_6 selectivity was increased from 4.7 to 5.5.

The gas permeation behavior through a glassy polymeric membrane is typically described by the solution-diffusion model, that is, gas permeability is determined by the solubility and diffusivity of the gas. The diffusion coefficients of penetrants often change less than the solubility coefficients with changing feed pressure, so that the increase of SF_6 permeance is larger than that of N_2 permeance due to the higher solubility of SF_6 as a condensable gas in the membrane. The diffusion coefficient always increases with temperature; however, the solubility coefficient is vice versa, so selectivity increases with temperature although SF_6 permeance is increased.

3. N₂/SF₆ Mixture Gas Separation

3-1. Effects of Pressure Difference and Retentate Flow Rate

We implemented a fixed temperature of 25 °C and used well-mixed binary mixture gas (10 vol% SF_6 concentration). The ranges of the pressure difference and retentate flow rate were 3-10 kg/cm²
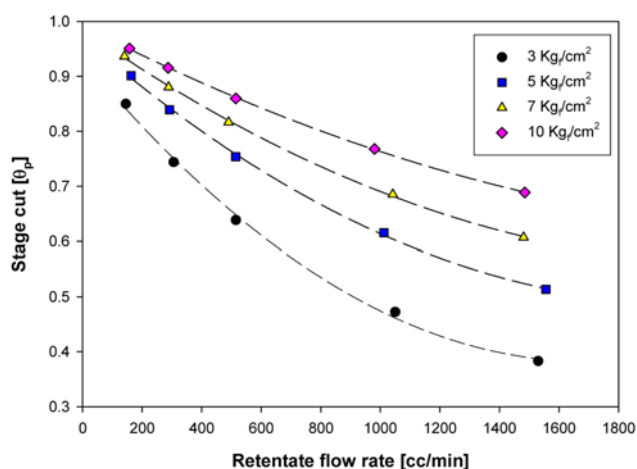
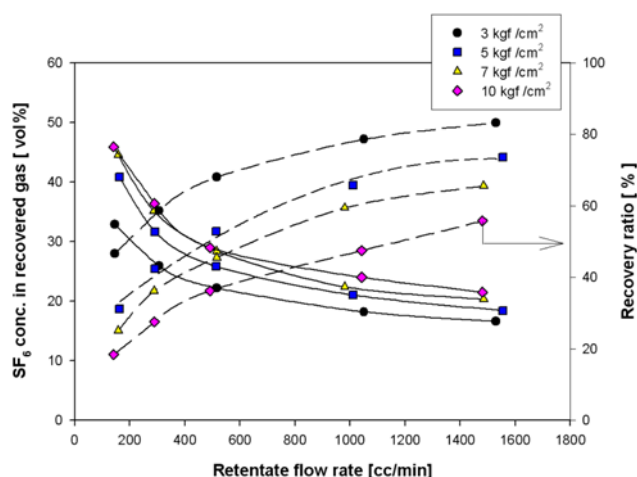**Fig. 5. SF₆ purity and recovery ratio in recovered gas according to pressure and retentate flow rate at 25 °C.**

and 150-1,500 cc/min, respectively. The experiment was on countercurrent and used a back pressure regulator to control the retentate flow rate and to make the stage cut different.

Fig. 4 shows that the stage cut has a negative correlation with the pressure difference and retentate flow rate. Fig. 5 displays the graph of the SF_6 concentration in the retentate side and module's recovery ratio. At 10 kg/cm² of Δp and 150 cc/min of retentate flow rate, we measured a 45.9 vol% of SF_6 (highest) and 18.4% of recovery ratio (lowest).

At a fixed pressure, when the stage cut is low, the purity of the gas that has high permeation speed relatively increases in the permeate side. For increasing the stage cut, the driving force of penetrants against the membrane would be increased, and this brings a coercive permeation. Therefore, gas that has low permeation speed is gathered in the retentate side. That is, the increasing of Δp and the decreasing of the retentate flow rate affects the permeation of N_2, concentration increase of SF_6, and recovery ratio decrease.

3-2. Effects of Temperature and Retentate Flow Rate

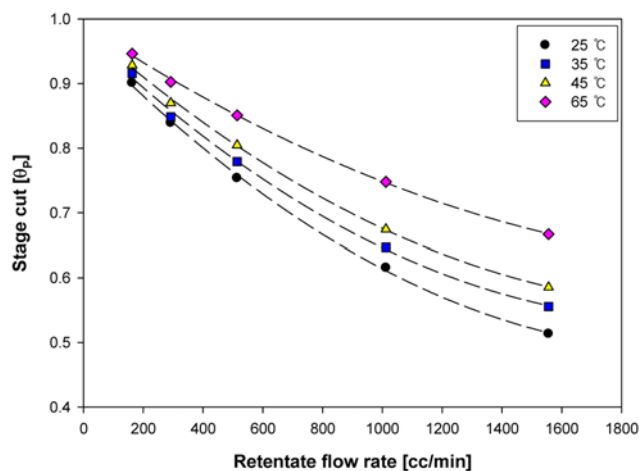Next, an experiment was conducted according to temperature

Fig. 4. Stage cut according to pressure difference and retentate flow rate at 25 °C.
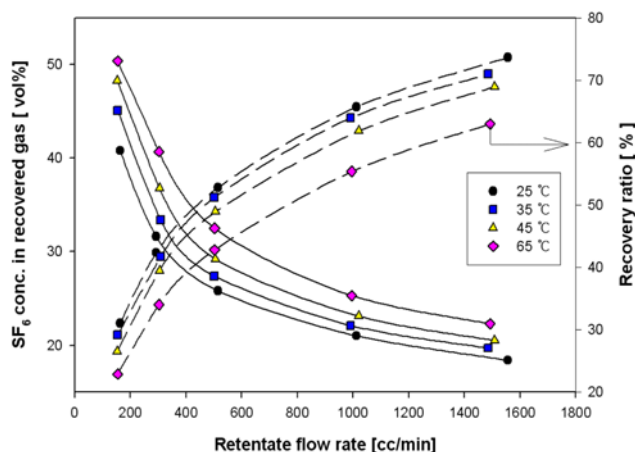
Fig. 6. Stage cut according to temperature and retentate flow rate at 5 kg/cm².

Fig. 7. SF$_6$ purity and recovery ratio in recovered gas according to temperature and retentate flow rate at 5 kg$_f$/cm^2.

(25-65 $^\circ$C) and retentate flow rate (150-1,500 cc/min) under 5 kg/cm^2 of pressure difference. The stage cut increased following the increase in temperature, as shown in Fig. 6.

Fig. 7 shows the relation between the SF$_6$ concentration in recovered gas and the recovery ratio according to the temperature and retentate flow rate. According to the increasing temperature from 25 to 65 $^\circ$C, SF$_6$ conc. in recovered gas was increased from 40.8 to 50.4 vol% (24% rate of increase), but the recovered ratio was decreased from 31.0 to 22.9% in 150 cc/min retentate flow rate.

As with the data in N$_2$, SF$_6$ single gas permeation, N$_2$/SF$_6$ selectivity had positive correlation with temperature, meaning that the permeation speed of N$_2$ is much higher because it has high activation energy. Therefore, in the separation of mixture gas, the flux of N$_2$ through the membrane will increase according to increasing temperature, but, due to both permeations of N$_2$, SF$_6$ increasing, the recovery ratios are decreased.

CONCLUSION

Using a PESf hollow fiber membrane, we wanted to separate SF$_6$, which has high global warming potential, in N$_2$/SF$_6$ binary mixture gas.

1) We fabricated a hollow fiber membrane using dry-wet phase inversion and observed a cross-section of a membrane that has an asymmetrical structure with a close selective layer on the surface and sponge-like structures in the fiber. In the fabrication stage, it was post-treated to improve permeance, and it was coated with PDMS for removing surface defects and pin-hole. The finished module had a 0.67 m^2 effective cross-sectional area.

2) In N$_2$, SF$_6$ single gas permeation, an experiment was conducted in conditions of a 25-65 $^\circ$C temperature range and a 3-10 kg/cm^2 pressure difference range. As a result, the SF$_6$ permeance growth was large relatively according to the pressure difference, but N$_2$'s permeance growth was larger according to the temperature. Therefore, the N$_2$/SF$_6$ selectivity was increased due to the increasing temperature or the decreasing pressure difference.

3) For the separation mixture gas, we used well-mixed binary mixture gas (10 vol% SF$_6$ purity) and checked the relations between the concentration of SF$_6$ in the retentate side and the recovery ratio according to temperature, pressure difference, and retentate flow rate.

4) In a fixed temperature condition, the SF$_6$ concentration in recovered gas was increased according to the increasing pressure difference in a regular retentate flow rate. However, the recovery ratio was decreased under the same conditions. At 25 $^\circ$C, 150 cc/min retentate flow rate, 10 kg/cm^2 pressure difference conditions, 45.9 vol% of SF$_6$ concentration was marked as the best value.

5) In a fixed pressure difference condition, the SF$_6$ concentration in recovered gas was increased according to increasing temperature in a regular retentate flow rate because of the improving permeance of N$_2$. At 65 $^\circ$C, 150 cc/min retentate flow rate, 5 kg/cm^2 pressure difference conditions, 50.4 vol% of SF$_6$ concentration was marked as the best value, which means that increasing temperature is advantageous to improve a membrane's separation ability because of N$_2$'s selective separation.

We were able to obtain highly pure SF$_6$ by increasing the pressure difference and temperature using a PESf hollow fiber membrane. However, it was necessary to use multi-stage separation for higher purity of gas and recovery ratio. We can use this separation data using a single module for future research by using multi-stage separation.

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