CHAPTER III
EXPERIMENTAL

3.1 Materials

The following materials were kindly provided by UOP, A honeywell Company, USA; 4A zeolite (NaA), gamma-alumina, activated carbon and Matrimid 5218 polymer. N-methyl-2-pyrrolidinone (NMP) and 1, 3-dioxolane from Sigma-Aldrich were used as the solvents. The tested gases were carbon dioxide (CO_2), methane (CH_4) and hydrogen (H_2) which were obtained from Airgas Inc., for the tests carried out in UOP lab. NaA zeolites were calcined at 250 °C for 4 h to remove any impurities before use.

For PPC lab, n-methyl-2-pyrrolidinone (boiling point = 202 °C) from Labscan Co., Ltd and 1, 3-dioxolane (boiling point = 75-76 °C/1.013 hPa) from Sigma-Aldrich were used. In this study, N_2 and CO_2 from Praxair and CH_4 from Labgaz Co., Ltd (Thailand) were used as the tested gases for all membranes. All tested gases are in a high purity (HP) grade (99.99%) and used as received.

3.2 Methodology

3.2.1 Methodology at UOP

3.2.1.1 Preparing of Dense Matrimid Membranes

All dense membranes were prepared on the basis of 20 wt.% Matrimid in a mixture of NMP and 1, 3-dioxolane (1:1 w/w) by the solution-casting technique. The solution was stirred at room temperature for 2 h by a mechanical mixer and was subsequently filtered over a 10 μm metal filter to remove non-dissolved residual materials. Afterwards, the solution was degassed overnight for the complete degassing. Then the bubble free solution was cast on a clean glass plate using a casting knife at 55 °C on a hot plate and heated overnight to evaporate the solvents slowly, as covered with aluminum foil. The thickness of casting layer was adjusted by a casting knife at 20 mil (508 μm). The membrane was then peeled off

from the glass plate and placed between two filter papers in a vacuum oven at 150 °C for 48 h to remove the residual solvent from the membrane.

3.2.1.2 Preparation of Mixed Matrix Membranes

All steps were followed the dense Matrimid membrane preparation except for dispersion of inorganic fillers into Matrimid polymer. The solution-casting method was used to fabricate 15 wt.% and 25 wt.% inorganic filler-Matrimid mixed matrix membranes (MMMs). MMMs were prepared based on 20 wt.% particles (inorganic fillers and Matrimid) in the total solution of 40 g. Inorganic particles were dispersed in NMP and 1, 3-dioxolane and mixed for 1 h. Then, a half of the polymer was added to the solution as a primer to increase adhesion between the polymer and particles. After 0.5 h mixing, the remaining polymer was added and the solution was stirred for another 1 h to form a uniform mixture. The resultant solution was kept at room temperature without mixing for 4 h in order to have complete degassing. The casting, evaporation and drying steps of mixed matrix membranes were the same as those of dense Matrimid membranes.

3.2.2 Methodology at PPC

3.2.2.1 Preparation of Dense Matrimid Membranes

All dense membranes were prepared on the basis of 20 wt.% Matrimid in 1, 3-dioxolane solvent by the solution-casting technique. The solution was stirred at room temperature for 12 h by using a magnetic stirrer to get homogeneous solution. The solution was degassed by a vacuum pump for 0.5 h. Afterwards, the bubble free solution was cast on a clean glass plate using a casting knife at 10 mil (254 μm). The nascent membrane was dried in the box saturated with the solvent for 24 h in order to delay solvent evaporation and allowed to evaporate slowly at 80 °C for 12 h.

3.2.2.2 Preparation of Mixed Matrix Membranes

The procedures for fabricating MMMs were similar to those of the dense Matrimid membrane except for dispersion of inorganic fillers into Matrimid polymer. Inorganic filler was dissolved in 1, 3-dioxolane and stirred for 12 h. Then 15 wt. % of the polymer was added to the solution and stirred for 6 h in order to increase the compatibility between inorganic particles and polymer and to

minimize the aggregation of inorganic particles. The remaining polymer was added and the solution was stirred for another 12 h to disperse inorganic filler completely. The procedures of degassing, casting, evaporation and drying for mixed matrix membranes were the same as those of dense Matrimid membranes.

3.2.3 Differences in Membrane Preparation at UOP and PPC

Typically, γ-Al$_2$O$_3$ incorporated MMMs in UOP lab suffered from defects, non-selective interfacial voids. Therefore, it is imperative to alleviate such a phenomenon by the alternation of fabrication method. The different fabrication features in UOP lab and PPC lab are shown in Table 3.1.

Table 3.1 The different fabrication features in UOP lab and PPC lab

Fabrication Feature	UOP Lab	PPC Lab
Types of Solvent	NMP and 1, 3-dioxolane	1, 3-dioxolane
Priming	50 wt.% of the total polymer	15 wt.% of the total polymer
Casting Thickness	20 mil	10 mil
Evaporation	55 °C on a hot plate overnight	in the box saturated with the solvent for 24 h
Drying	in a vacuum oven at 150 °C for 48 h	in an oven at 80 °C for 12 h

3.2.4 Membrane Characterization

Scanning electron microscopy (SEM) was performed using a FESEM (Hitachi S4800). Samples were prepared by the freeze-fracture of the membrane in liquid nitrogen and subsequent sputter-coating with a thin layer of platinum. Mitutoyo digital micrometer was used to measure the thickness of membranes. The thickness of the tested membranes was in the range of 2.6-3.4 mil depending on the inorganic filler loading.

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3.2.5 Gas Permeability Measurements

3.2.5.1 Gas Permeability Measurements in UOP Lab

Single gas permeation measurements of CO_2, CH_4 and H_2 were carried out using a dense film permeation unit to measure permeabilities and diffusivities by a constant volume method, a time-lag method. This method measures a pressure increase in a constant downstream volume as a function of time to determine permeability. For each measurement, a 9.58 cm^2 membrane was mounted in a dense film test cell at 50 $^\circ$C and the whole system was kept under vacuum overnight. Afterwards, permeability measurements were conducted by introducing a single gas at an upstream pressure of 100 psig. Upstream and downstream pressures were recorded, and the steady-state slope of the downstream pressure versus time was determined from the acquired data. The permeability of gas through membrane was determined by the constant volume method from the Equation (3.1). The ideal selectivity was then calculated from the ratio of the single gas permeability. The schematic diagram of the dense film permeation unit and dense film test cell is shown in Figure 3.1.

Permeability shown in Equation (3.1) is expressed in gas permeation units, Barrer, where P (Barrer) is 10^{-10} cm^3 (STP) cm/ cm^2 .sec.cmHg.

$$P_i = k(dp_2/dt)(V_2/p_1)l \tag{3.1}$$

where

P_i = permeability of gas (cm^3(STP)·cm/cm^2·sec·cmHg)

l = thickness of membrane (cm)

V_2 = volume on the permeate side of membrane (cm^3)

dp_2/dt = pressure difference across membrane (cmHg/sec)

k = 1.16034 × 10^{-3}/ cmHg·cm^2

US = Upstream
DS = Downstream
INT = Internal Downstream
PG = Pressure Gauge
PT = Pressure Transducer

Figure 3.1 Schematic diagram of the dense film permeation unit and dense film test cell (Youchang, 2006).

3.2.5.2 Gas Permeability Measurements in PPC Lab

In this study, N_2 and CO_2 (Praxair) and CH_4 (Labgaz) were used as the tested gases for all membranes. All tested gases are in a high purity (HP) grade and used as received.

The schematic diagram of gas permeability measurement including gas sources, a membrane testing unit, and a gas flow meter is shown in Figure 3.2. Schematic of the membrane testing unit is shown in Figure 3.3.

Single gas permeability of CO_2, N_2 and CH_4 will be determined at 25 °C in sequence by using a gas permeation testing unit in which the membrane is placed on a porous metal plate and pressurized to the desired pressure at the feed side. The effective area of the membrane on a porous plate is 35.26 cm^2. The pressure difference across the membrane will be maintained at 100 psi. Once reaching the steady-state, individual gas flow rates will be measured using a soap bubble flow meter. The attained data are used to calculate the gas permeance and selectivity.

The permeance or pressure normalized flux of component *i* is expressed as a thickness normalized permeation rate. Permeance shown in Equation

(3.2) is expressed in gas permeation units, GPU, where GPU $= 1 \times 10^{-6}$ cm^3 (STP)/cm^2·sec·cmHg.

$$\left(\frac{P}{\delta}\right)_i = \frac{Q_i \times 14.7 \times 10^6}{(A) \times (\Delta P) \times 76} \qquad (3.2)$$

where

$\left(\dfrac{P}{\delta}\right)_i$ = permeance of gas i (GPU)

P = permeability of gas i (cm^3(STP)·cm/cm^2·sec·cmHg)

δ = thickness of membrane (cm)

Q_i = volumetric flow rate of gas i (cm^3/sec)

A = area of membrane (cm^2)

ΔP = pressure difference across membrane (psi)

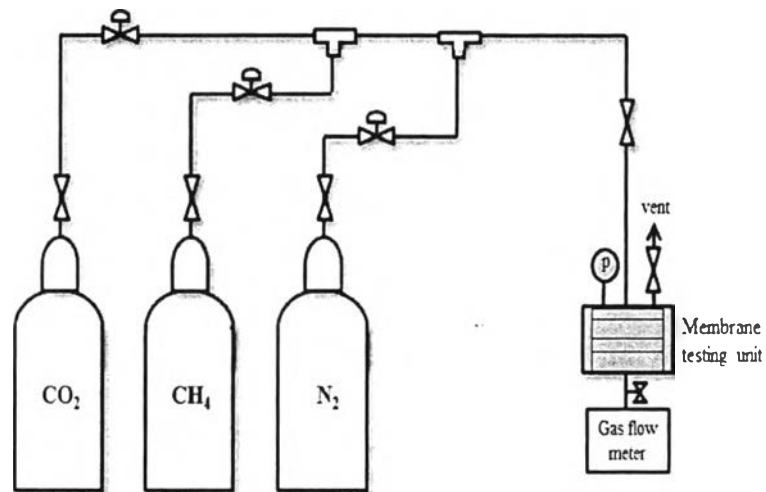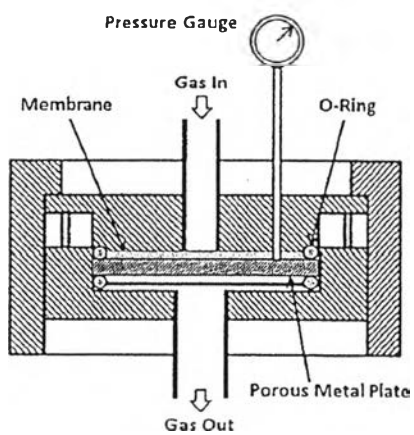**Figure 3.2** Schematic diagram of the experimental setup for determining a gas permeability.

Figure 3.3 Schematic of the membrane testing unit.