CHAPTER III
EXPERIMENTAL

3.1 Materials

Polyetherimide (Ultem®1000) supplied by UOP LLC., USA was used as the continuous matrix phase in MMMs. In this project, two types of metal organic frameworks (MOFs) selected as a solid phase were Basolite™ C300 (MOF-199) and Basolite® Z1200 (ZIF-8) manufactured by Sigma Aldrich Co., Ltd. Anhydrous N-methyl-2-pyrolidone (NMP, 99.5 %) purchased from Labscan Co., Ltd. was used as solvent. N_2 (99.99%) and CO_2 (99.99%) purchased from Praxair Inc. and CH_4 (99.99%) purchased from Linde (Thailand) PLC. were used as tested gases for all membranes.

3.2 Methodology

3.2.1 Membrane Preparation

Before membrane preparation, Ultem®1000 polymer and MOFs (ZIF-8 and MOF-199) were dried at 110°C for 12 h in an oven.

3.2.1.1 Dense Membrane

All membranes were prepared by the solution-casting technique. An Ultem solution was prepared by mixing 13 wt% Ultem in NMP solvent. The solution was stirred at room temperature for 24 h to obtain a homogeneous solution. Afterwards, the solution was degassed by an ultrasonic bath for 30 min. The resulting bubble-free solution was cast onto a dust-free glass plate and adjusted its thickness at 22 µm using a casting-knife. The resultant solution was allowed to slowly dry for overnight until a film was formed on the glass plate. The film was dried and annealed at 80°C for 12 h in an oven in order to remove NMP solvent off the thin film sheet. The dried membrane was placed between two glass plates at room temperature for 48 h to prevent the curling of the film, and allowed it to form a stable membrane.

3.2.1.2 Mixed Matrix Membranes

All steps were followed the dense membrane preparation except that each MOF was added into NMP solvent before the Ultem powder. Approximately 10% of the total amount of Ultem powder was added to the MOF/NMP solution to "prime" the MOF particles. In fact, the priming technique which is the addition of low amounts of polymer to the filler suspension before incorporating the particles into the polymer solution is believed to make the particles more compatible with the bulk film polymer in which it promotes greater affinity between the filler and the polymer thus improving the transport properties of the MMMs (Nik *et al.*, 2012). The resultant slurry was stirred for 6 h. After homogenization, the remaining 90% of Ultem powder was added and the mixture was stirred for overnight. The concentration of each MOF was varied from 10 wt% to 30 wt% with an interval of 10% on a solvent-free basis as determined by Eq. (3.1).

$$MOF\ loading\ (wt\%) = \left[\frac{wt.MOF}{wt.MOF + wt.polymer} \right] \times 100 \qquad (3.1)$$

Finally, all prepared membranes were cut into circles (67 mm in diameter) in order to determining a gas permeability measurement.

3.2.2 Membrane Characterization

Scanning electron microscopy (SEM) was performed using a Hitachi TM3000 microscope. Samples were prepared by freeze-fracture of the membrane and subsequent sputter-coating with a thin layer of platinum. The thickness of tested membranes was determined using a PDN-20 digital gauge from Peacock.

3.2.3 Gas Permeability Measurements

In this study, N_2 (Praxair), CO_2 (Praxair) and CH_4 (Linde) were used as tested gases for all membranes. All tested gases are in a high purity (HP) grade (99.99%).

A schematic diagram of the experimental setup for a gas permeability measurement consisting of gas sources, a membrane testing unit, and a gas flow

meter is shown in Figure 3.1. Schematic of the membrane testing unit is shown in Figure 3.2.

Single gas permeability of N_2, CH_4 and CO_2 was determined at room temperature in sequence by using a gas permeation testing unit in which the membrane was placed on a porous metal plate and pressurized to the desired pressure at the feed side. The pressure difference across a membrane was initially maintained at 50 psi and consequently 100 psi for individual membranes. At steady-state, each gas flow rate was measured using a soap bubble flow meter. The attained data were used to determine the gas permeance and selectivity.

The permeance or pressure normalized flux of component i is expressed as a thickness normalized permeation rate in gas permeation units, GPU, where 1 GPU = 10^{-6} cm^3 (STP) cm^{-2} s^{-1} $cmHg^{-1}$. The permeance of each gas was calculated based on the following equation:

$$\left(\frac{P}{\delta}\right)_i = \frac{Q_i \times 14.7 \times 10^6}{(A) \times (\Delta P) \times 76}$$ (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} s^{-1} $cmHg^{-1}$)

δ = thickness of membrane (cm)

Q_i = volumetric flow rate of gas i (cm^3 s^{-1})

A = area of membrane (cm^2)

ΔP = pressure difference across membrane (psi)

The gas selectivity ($\alpha_{A/B}$) was calculated by the following relationship:

$$\alpha_{A/B} = \frac{P_A}{P_B}$$ (3.3)

where P_A and P_B are the permeabilities of pure gas A and B that pass through the membrane, respectively.
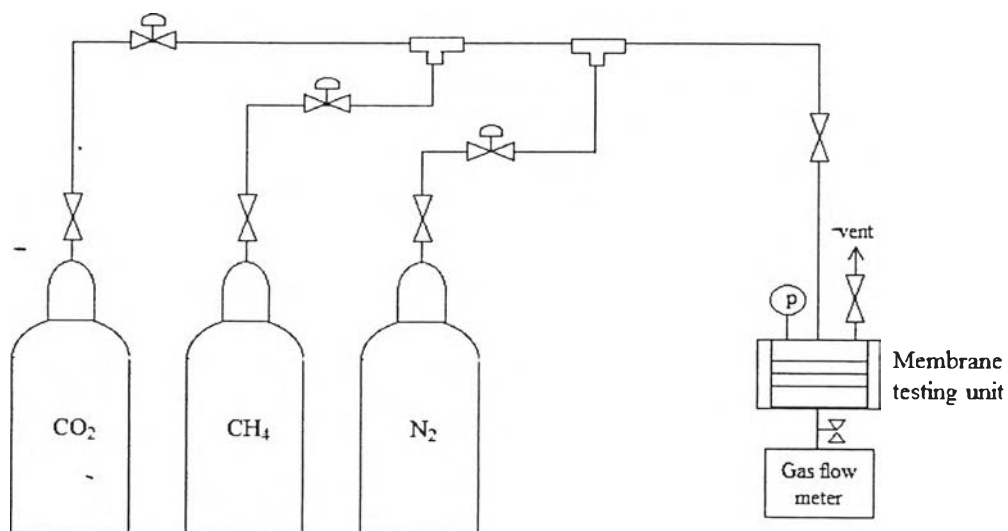

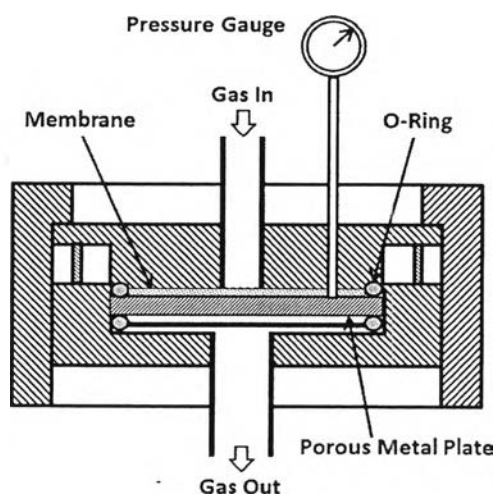**Figure 3.1** Schematic of the experimental setup for determining a gas permeability.

Figure 3.2 Schematic of the membrane testing unit.