Fabrication of 6FDA-based composite membranes loaded with MIL-125 (Ti) for CO₂/CH₄ separation

Nadia Hartini Suhaimi¹,², Yin Fong Yeong¹,², Thiam Leng Chew¹,², Mohamad Azmi Bustam¹,³, Norwahyu Jusoh¹,⁴

¹Chemical Engineering Department, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak.
²CO₂ Research Centre (CO2RES), R&D Building, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak.
³Centre of Research in Ionic Liquids (CORIL), Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak.
⁴Centre for Contaminant Control & Utilization (CenCoU), Chemical Engineering Department, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak.

E-mail: yinfong.yeong@utp.edu.my

Abstract. Carbon dioxide (CO₂) separation is necessary for natural gas purification to enhance the calorific value of methane gas (CH₄), besides reducing the corrosion risk in pipelines with the presence of water or moisture. This work focuses on the development of new combination of composite membrane materials containing titanium-based metal organic frameworks (MOFs) and 6FDA-based polymer for CO₂ and CH₄ gases permeation. The composite membranes were successfully fabricated by incorporating 0.5, 1.0, 3.0 and 5.0 wt% of MIL-125 (Ti) fillers into 6FDA-durene polymer by using solvent evaporation method. The resultant fillers and composite membranes were characterized by using different analytical tools including XRD, FESEM and EDX. Then, the permeability test was conducted by using single gas of CO₂ and CH₄. The results showed that composite membrane loaded with 5wt% of MIL-125(Ti) showed the highest CO₂ permeability of 814.9 Barrer, and CO₂/CH₄ ideal selectivity of 18.1 compared to pure 6FDA-durene membrane with CO₂ permeability of 510.3 Barrer and CO₂/CH₄ ideal selectivity of 8.6. It was found that the incorporation of fillers, MIL-125 (Ti) into 6FDA-durene polymer matrix led to the enhancement of gas permeation performance due to good compatibility between fillers and polymer matrix. Besides, the presence of organic ligand in MIL-125 (Ti) filler has potentially reduced the interfacial voids between the filler and polymer.

1. Introduction
In Malaysia, high CO₂ gas fields identified in PM313 and South West Luconia cluster located in peninsular and Sarawak, respectively with CO₂ content in the range of 28% – 87% [1]. The presence of carbon dioxide will reduce the calorific value of natural gas and also induced the corrosion of pipelines and equipment in the presence of water [2]. In addition, the CO₂ concentration allowed in pipeline specification is below 3% [3]. Therefore, it is crucial to separate CO₂ from CH₄ before compression and delivery. Various gas separation technology such as adsorption [4], absorption [5], cryogenic distillation
[6] and membrane technology[7] are widely reported in the literature and each of this technology possesses advantages and disadvantages.

Over the last decades, membrane technology received more attention due to low energy consumption, simple operation and high efficiency [8]. The development of membrane technology started with polymeric membranes [9], then inorganic membranes [10] and recently composite membranes or mixed matrix membranes [11]. Polymeric membrane offer few advantages such as easy to scale up, involved lower cost and simple fabrication, however it suffers from Robeson’s trade-off limit between permeability and selectivity [12]. This lead to the development of inorganic membrane because of their superior performance. However, inorganic membranes having difficulties for scale-up [13] beside high fabrication cost [14]. Due to these reasons, researches have been focused on the development of composite membranes or mixed matrix membranes by combining both characteristics of polymeric and inorganic membranes.

Recently, a new class of materials known as metal organic frameworks (MOFs) have been explored as the potential filler for the fabrication of composite membranes. MOFs usually demonstrate high surface area, high adsorption capacity, excellent chemical and thermal stability and flexible pore size [15-17]. In addition, MOFs fillers contain partially organic ligands which can improve polymer-filler adhesion, and thus lead to a better performance of composite membranes [6, 18]. Commonly reported MOFs used as a filler for the fabrication of composite membranes including ZIF-8 [19, 20], MIL-53 [13, 21-24], UIO-66 [25, 26], UIO-67 [27], MOF-199 [27], MIL-125 (Ti) [28] and MIL-101 [26, 29].

A highly porous titanium based MOF known as MIL-125 (Ti) is built up from cyclic octamers made from corner or edge sharing TiO$_5$(OH) octahedrons, connected to other 12 cyclic octamers through terephthalate ligands (BDC) [30, 31]. It has a quasi-cubic tetragonal structure in 3D arrangement of octahedral vacancies and tetrahedral cages with effective diameters of 12.5 Å and 6 Å [30]. Besides, MIL-125 (Ti) exhibits excellent thermal and water stability [28] as well as high porosity [32]. On the other hand, 6FDA-durene polyimide is chosen in this work because previous study [21, 27, 33] showed that fluorinated polyimide containing 6FDA displayed higher gases permeability compared to the other polymeric materials due to the presence of -C(CF$_3$)$_2$ groups.

Although there are several studies reported [28, 32] on the utilization of MIL-125 (Ti) as a filler in fabrication of composite membrane for gas separation, the incorporation of MIL-125 (Ti) into fluorinated polyimide is hardly found in the literature. Thus, in this work, MIL-125 (Ti)/6FDA-durene composite membranes were fabricated, characterized and the performance of the resultant membrane in CO$_2$/CH$_4$ separation was also tested.

2. Experimental

2.1. Materials

Synthesis of MIL-125 (Ti) fillers required pivalic acid (99%), N,N-dimethylformamide (DMF), terephthalic acid (98%), acetonitrile (99.8%) and tetraisopropyl orthotitanate (97%), which were purchased from Sigma Aldrich and used without further purification.

Synthesis of 6FDA-durene polyimide required two monomers including durene diamine (99%) and 4,4’(Hexafluoroisopropylidene) dipthalic anhydride (99%). Both monomers were purified by using re-crystallization in methanol and vacuum sublimation, respectively. Propionic anhydride (PA, ≥98%), triethylamine (TEA, ≥99%), methanol (CH$_3$OH≥99.9%), N-Methyl-2-pyrrolidone (NMP) and dichloromethane (DCM≥99.8%) were used as received. All chemicals were purchased from Merck.
Single gas carbon dioxide (CO$_2$, 99.9995% purity) and methane (CH$_4$, 99.9995% purity) used for gas permeation testing were purchased from Air Products Sdn. Bhd.

2.2. Synthesis of MIL-125 (Ti)
MIL-125 (Ti) fillers were synthesized by using hydrothermal growth method [28]. Firstly, 17.5 g of pivalic acid was dissolved in a mixture solution containing 125 mL of acetonitrile and 5 mL of tetraisopropyl orthotitanate. Next, the mixture solution was placed in a Teflon-lined autoclave reactor and heated at 100 °C for 84 h to obtain white crystals. The white crystals were filtered and dried in oven at 80 °C for 24 h. Then, 2.4 g of white crystals were dissolved in mixture solution containing 50 mL of methanol and 50 mL of DMF before mixed into a mixture solution containing 3 g of terephthalic acid and 75 mL of DMF. After that, the mixture solution was heated in an oven at 100 °C for 24 h and the white solid powder was recovered from the solution using centrifuge. Then, the resultant white solid powder was washed with methanol and DMF for several times before dried in oven at 60 °C for 24 h.

2.3. Synthesis of 6FDA-durene polyimide
The 6FDA-durene polyimide was synthesized using chemical imidization method as reported in literature [20]. Both monomers were dissolved in NMP and stirred for 24 h under nitrogen condition. Then, PA and TEA were added into the solution for chemical imidization. The polyimide solution was precipitated in methanol, washed with methanol for several times and dried at 150 °C under vacuum for 24 h.

2.4. Fabrication of pure and composite membranes
6FDA-durene and composite membranes were fabricated by using solution-casting method. A 2 w/v% polymer solution was dissolved in DCM. The solution was filtered using 5.0 µm PTFE membrane filter and cast on a petri dish. The resultant membrane was dried in an oven at 60 °C for 24 h. Then, continued dried in vacuum condition for 24 h at the same temperature before proceeded to thermal annealing procedure. The temperature was increased from 60 °C to 250 °C at a heating rate of 25 °C/hour. Once achieved 250 °C, the resultant membrane was kept in vacuum oven for 24 h.

On the other hand, composite membranes containing 6FDA-durene polymer with 0.5 wt%, 1.0 wt%, 3.0 wt% and 5.0 wt% of MIL-125 (Ti) fillers, respectively, were fabricated based on the method reported in the literature [34]. Filler and polymer were dissolved in DCM, separately. Filler suspension was stirred and sonicated alternately to disperse the fillers in DCM. Then, 10 wt% of polymer solution was added into fillers suspension by priming technique to induce the polymer-filler interface [35] before further stirred and sonicated. After sonication, the remaining polymer solution was added into the mixture and again further stirred and sonicated. Next, the mixture was stirred vigorously for 1 hour before cast onto a petri dish. After casting, the petri dish was immediately covered by the glass plate for slow solvent evaporation. After 24 h, the resultant membrane was peeled off and dried in oven at 60 °C before proceeding to thermal annealing procedure used for the fabrication of 6FDA-durene membrane. The summary of membrane samples fabricated in this work is shown in Table 1.

| Sample | Composite Membrane | Filler loading (%) |
|--------|--------------------|--------------------|
| M0     | 6FDA-durene        | 0                  |
| M1     | 0.5 wt% MIL-125 (Ti)/6FDA-durene | 0.5               |
| M2     | 1.0 wt% MIL-125 (Ti)/6FDA-durene | 1.0               |
| M3     | 3.0 wt% MIL-125 (Ti)/6FDA-durene | 3.0               |
| M4     | 5.0 wt% MIL-125 (Ti)/6FDA-durene | 5.0               |
2.5. Characterization
The crystal structure and phase purity of MIL-125 (Ti) fillers was analyzed via X-Ray diffractometer (X’Pert3 Powder, Panalytical) at room temperature by using Cu Kα as a radiation source with a radiation wavelength \( \lambda = 1.54059 \, \text{Å} \) in 2\( \theta \) range of 5 – 40° at a step size 0.02°. The morphology of the fillers was investigated by using field emission scanning electron microscopy (Zeiss Supra 55VP) operated at 10 kV under vacuum condition. The fillers sample was pasted on top of the sample-holder surface using a double-sided carbon tape prior to imaging. On the other hand, the dispersion of filler in the resultant membranes was observed through EDX mapping by using energy dispersion X-ray (EDX) (Oxford Instrument Inca).

2.6. Gas permeations measurements
Gas permeation test was conducted using permeation equipment described elsewhere [36]. The membrane sample was placed onto the membrane sample test cell with effective area of 1.767 cm\(^2\). The gas permeation testing was conducted at feed pressure of 3.5 bar and room temperature. The gas permeability was calculated using equation (1) as follows [37]:

\[
P = \frac{V_p t}{A_m (p_f - p_l)}
\]

where \( P \) is the gas permeability (Barrer), \( t \) is thickness of membrane (cm), \( V_p \) is the permeate flowrate (cm\(^3\)(STP)/s), \( A_m \) is the area of membrane surface (cm\(^2\)), \( p_f \) and \( p_l \) are the pressure of feed and permeate, respectively (cmHg). The CO\(_2\)/CH\(_4\) gas pair selectivity of membrane was calculated by using equation (2) as follows [37]:

\[
\alpha_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}}
\]

where \( \alpha \) indicates the CO\(_2\)/CH\(_4\) gas pair selectivity and \( P \) is the permeability of gases (Barrer).

3. Results and Discussion

3.1. X-ray Diffraction (XRD)
Figure 1 shows the X-ray diffraction pattern obtained for MIL-125 (Ti) fillers. Referring to Figure 1, the X-ray diffraction pattern obtained is consistent with those result reported in the literature [28, 38]. The diffraction peaks of MIL-125 (Ti) at 2\( \theta \) values are 6.8°, 9.8°, 11.7°, 15.1°, 15.5°, 16.6°, 17.9°, 19.1°, 19.6° and 22.7°, which confirmed the formation of highly crystalline MIL-125 (Ti) fillers.
Figure 1. X-ray diffraction pattern of MIL-125 (Ti) filler synthesized in this work

3.2. Field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) spectroscopy mapping

The morphology of MIL-125 (Ti) fillers and the resultant membranes were characterized by using field emission scanning electron microscope (FESEM) and the images are shown in Figure 3(a-f). Referring to Figure 3 (a), MIL-125 (Ti) fillers demonstrate well-defined crystalline block-like particles with diameter of 0.9 – 1.3 µm are obtained. The results are in agreement with those result reported in literature [38].

Figure 3 (b-f) presents the FESEM images of 6FDA-duce and MIL-125 (Ti)/6FDA-durene composite membranes. Referring to Figure 3 (c-f), the presence of MIL-125 (Ti) fillers in the polymer matrix are observed. The presence of fillers is more visible with the higher loading of MIL-125 (Ti) fillers. Furthermore, the MIL-125 (Ti) are encapsulated in 6FDA-durene polymer. In addition, the formation of concentric cavities exhibited strong interfacial contact between MIL-125 (Ti) fillers and 6FDA-durene polymer matrix [39].
The resultant composite membranes were further analysed by using energy dispersive X-ray (EDX) spectroscopy mapping for the distribution of MIL-125 (Ti) fillers and the results are shown in Figure 3. Referring to Figure 3, the resultant composite membranes demonstrate well distribution and no obvious agglomeration were observed.

3.3. Gas permeation performances

The CO$_2$ permeability and CO$_2$/CH$_4$ ideal selectivity of the composite membranes are shown in Figure 4. Based on Figure 4, CO$_2$ permeability and CO$_2$/CH$_4$ ideal selectivity increase as the loading of MIL-125 (Ti) increases. At loading of 5 wt% of MIL-125 (Ti), the composite membrane exhibited the highest CO$_2$ permeability and CO$_2$/CH$_4$ ideal selectivity compared to the other composite membrane fabricated in this work.

The CO$_2$ permeability obtained for MIL-125 (Ti)/6FDA-durene composite membranes loaded with 0.5 wt% to 5 wt% MIL-125 (Ti) fillers were in the range of 642.5 Barrer to 814.9 Barrer, which is higher than CO$_2$ permeability of 6FDA-durene membrane of 510.3 Barrer. This increment is mainly due to the incorporation of MIL-125 (Ti) filler into polymer matrix which has changed the polymer chain packing and enhanced the free volume in the composite membrane which resulted in better gas permeability [19, 34]. In addition, the introduction of MIL-125 (Ti) fillers into the polymer matrix may increase the inter-segmental spacing between polymer chains near the particles, which lead to the disturbance of the polymer chain packing [40, 41]. Besides, 6FDA-durene polyimide exhibits higher gas permeability due to the presence of -C(CF$_3$)$_2$ group in the dianhydride which restricted the rotation of adjacent phenyl rings, and thus, better interaction with non-polar CO$_2$ could be achieved [21]. In addition, CO$_2$/CH$_4$ ideal selectivity increased with MIL-125 (Ti) fillers loading from 8.6 for 6FDA-durene to 18.1 for the membrane loaded with 5 wt% of MIL-125 (Ti). The improved gas permeation performance of the composite membranes is due to the presence of organic linkages in the MOFs filler, which improved compatibility between the filler and polymer matrix, and thus, reduced the interfacial voids between the filler and polymer matrix [23].
Figure 4. CO\textsubscript{2} permeability and CO\textsubscript{2}/CH\textsubscript{4} ideal selectivity of composite membranes

Figure 5 compared the gas permeation performance obtained in this work with the Robeson plot. It can be seen from Figure 5 that pure 6FDA-durene membrane (M0) lies below 1991 Robeson upper bound limit. However, incorporation of MIL-125 (Ti) fillers into 6FDA-durene polyimide resulted in the increment of gas permeation performance closer to the 1991 Robeson upper bound limit. Besides, composite membrane loaded with 3.0 wt% and 5.0 wt% of filler successfully surpassed the 1991 Robeson upper bound limit. In this work, composite membrane incorporated with 5 wt% MIL-125 (Ti) fillers showed the highest gas permeation performance, with CO\textsubscript{2} permeability of 814.9 Barrer and CO\textsubscript{2}/CH\textsubscript{4} ideal selectivity of 18. From the results obtained, it can be concluded that the incorporation of MIL-125 (Ti) could enhance the gas permeation performance of 6FDA-durene membrane, mainly due to improved polymer-filler interface morphology.

Figure 5. CO\textsubscript{2}/CH\textsubscript{4} Robeson plot of composite membranes

4. Conclusion
Composite membranes containing different loadings of MIL-125 (Ti) fillers were successfully fabricated using solvent evaporation method. FESEM results showed that the MIL-125 (Ti) fillers were encapsulated in 6FDA-durene polyimide with the presence of concentric cavities. Besides, the well
distribution of fillers without significant agglomeration were confirmed by EDX mapping. The CO₂ permeability and CO₂/CH₄ selectivity showed increasing trends as the loading of fillers increased up to 5 wt%. Both increment in CO₂ permeability and CO₂/CH₄ selectivity could be due to the presence of MIL-125 (Ti) fillers as a CO₂ selective materials which increased the CO₂ solubility and provided more free volume in the membrane. However, the performance of membrane loaded with 5 wt% of MIL-125 (Ti) was only able to surpass the Robeson upper bound 1991. Therefore, future work has directed on the fabrication of composite membrane by using amine functionalization MIL-125 (Ti) as filler.

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