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Research Article

# The CO<sub>2</sub>/CH<sub>4</sub> Separation Potential of ZIF-8/Polysulfone Mixed Matrix Membranes for Biogas Upgradation Process

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**ABSTRACT.** Biogas is a renewable energy that has been explored widely in Indonesia to substitute non-renewable energy. However, the presence of certain gas, such as carbon dioxide (CO<sub>2</sub>), can decrease the calorific value and generate greenhouse gas. Hence, the separation of CO<sub>2</sub> from methane (CH<sub>4</sub>) occurs as a crucial step to improve the utilization of biogas. The separation of CH<sub>4</sub>/CO<sub>2</sub> can be conducted using a polymeric membrane that needs no chemical, hence considered as an environmentally friendly technique. However, the utilization of polymeric membrane in gas separation processes is hampered by the trade-off between gas throughput and selectivity. To solve this problem, the incorporation of inorganic particles, such as Zeolitic Imidazolate Framework-8 (ZIF-8) particles, into the polymer matrix to improve the gas separation performance of the membrane has been conducted recently. In this research, ZIF-8 has been incorporated into Polysulfone matrix to form ZIF-8/Polysulfone-based membrane by simple blending and phase inversion techniques in flat sheet configuration. The pure gas permeation tests showed an increase in gas permeability (26 Barrer compared to 17 Barrer) after the inclusion of ZIF-8 particles with a slight decrease in CO<sub>2</sub>/CH<sub>4</sub> selectivity for particle loading more than 15wt. %. Therefore, the membrane with 15wt. % of particles showed the best performance in terms of gas selectivity. This result was due to the aggregation of ZIF-8 particles at particle loading higher than 15wt. %. Chemical analysis indicated an interaction between filler and polymer, and there were increases in the degree of crystallinity after the incorporation of ZIF-8.

**Keywords:** Biogas, biomethane, ZIF-8/Polysulfone, mixed matrix membranes, CO<sub>2</sub>/CH<sub>4</sub> gas

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## 1. Introduction

Polymeric-membrane-based gas separation process has received considerable attention in recent years for natural gas sweetening, CO<sub>2</sub> removal from the fossil-fuel power station flue gas, and biogas upgradation processes due to its simple operation, easy to scale up, and potentially competitive cost (Sutrisna *et al.* 2017). Despite of many advantages for gas separation membranes, there exists a gas permeability-selectivity trade-off, particularly for the polymer-based membranes. The trade-off upper bound was compiled by Robeson in 1991 by plotting the logarithmic of gas permeability and selectivity of different gas pairs for the performance of existing gas separation membranes (Robeson 1991). The data was then updated in 2008 and the latest CO<sub>2</sub>/CH<sub>4</sub> data was presented in 2015 (Robeson 2008, Lin and Yavari 2015) with the rapid development of new materials and membranes.

One way to improve the performance of the polymeric gas separation membranes beyond the upper bound is to incorporate inorganic nanofillers within the polymer matrix, which is also known as mixed matrix membranes (MMMs). Compared with an inorganic coating on polymer membranes, the MMMs are relatively simple to prepare

thus considered a promising solution for large-scale practical applications (Aroon *et al.* 2010). For its successful implementation, several aspects need to be carefully considered: the selection of polymer and inorganic materials for membrane preparation, the regulation of the inorganic-polymer interfaces during the membrane fabrication process, the understanding of membrane property change and the gas transport mechanism within the mixed matrix membrane (Sutrisna and Savitri 2020). On the other hand, it is also very important to evaluate the long-term gas separation performance of the membrane for industrial applications, particularly their sustained performance under high feed pressure against membrane plasticization.

The conventional blending technique is the most commonly used approach to prepare MMMs (Sutrisna *et al.* 2017). One of the major issues with the blending technique is the difficulty to increase the inorganic filler loadings in the MMMs as the membranes will be very brittle. With low particle loadings, the gas transport behaviour in the membrane structure will still be dominated by the polymer matrix rather than the inorganic fillers. Most MMMs are synthesized in dense flat sheet form as this form of membrane is easy to fabricate

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and also can ensure the formation of defect-free membrane, which is a very important aspect for gas separation membranes. In addition to its simple fabrication process, dense flat MMMs can only produce low gas permeability or permeance due to its low surface area.

To synthesize MMMs, various inorganic particles have been utilized, including zeolite, activated carbon, carbon nanotubes, metal-organic frameworks, and coordination organic frameworks (Aroon *et al.* 2010 and Prasetya *et al.* 2020). In general, the particles used for MMMs can be classified as porous and non-porous particles. The main problem that can occur during MMMs synthesis is the incompatibility between the polymer and particles, especially for pure inorganic particles. In recent years, Metal-Organic Frameworks (MOFs) have been received a growing interest from many researchers as potential fillers in mixed matrix membranes. MOFs contain metal cations connected by organic-linker. MOFs have coordination-network and bonding, which make them less stiff and brittle than zeolite. So, it is considered that MOFs are able to show flexibility in terms of the gate opening and linker dynamics (Sutrisna *et al.* 2017). There are more than hundreds of MOFs structures that have been synthesized until now (Tran *et al.* 2020a,b; Tran *et al.* 2019a,b) and it is a big challenge to choose suitable MOFs that will be used as the filler in MMMs.

ZIFs materials are investigated more widely by many researchers as gas separation membranes or filler for mixed matrix membranes than any other MOFs because of their framework flexibility and high chemical and thermal stability (Sutrisna *et al.* 2020a). The bonding in MOFs is a coordination bonding that is weaker than covalent bonding in zeolite. This means that the bonding between metal node and organic-linker is not kinetically stable. This instability means that substitution by other ligands such as water might happen. However, for some MOFs like ZIF-8, ZIF-11, and ZIF-69 the stability of their structure can be maintained even in boiling solvents like benzene and water (Jeazet *et al.* 2012). Hydrophobic ZIF-8 with sodalite (SOD) topology connecting Zn<sup>2+</sup> metal and organic imidazolate linker is reported has 3.4 Å aperture diameter and it can retain its structure at the temperature up to 400°C. ZIF-8 has properties that make it considered as the most hydrolytically stable porous coordination polymer (Song *et al.* 2012). However, Zhang, *et al.* recently reported the effective aperture size of ZIF-8 particles is 4.0 to 4.2 Å (Zhang *et al.* 2012). Because of this flexibility, ZIFs can be selected to increase the permeability of polymeric-membrane in separating gas mixtures. To be utilized as filler inside MMMs, ZIF-8 has some advantages such as the organic part of ZIF-8 makes it easy to mix with polymer matrix as well as its porous nature that can enhance the gas permeability through the membrane. In addition to the versatility and high porosity of ZIF-8 to be incorporated into the polymer matrix, there are several studies studied the synthesis of ZIF-8/Polysulfone-based mixed matrix membranes (Nordin *et al.* 2015 and Mei *et al.* 2020). Previous studies mainly utilized ZIF-8 nanoparticles into the mixed matrix membranes; however, the particle loadings were relatively small (Nordin *et al.* 2015 and Mei *et al.* 2020). Hence, it is very useful to study and analyse the effect of higher particle loadings on the gas separation performance of the membranes. This study, hence, proposes a method to fabricate and test the ZIF-

8/Polysulfone-based mixed matrix membranes at higher loadings than previous studies. Furthermore, the effects of the ZIF-8 inclusion into the polymer matrix on the properties of the polymer are the focus of this study.

## 2. Materials and Methods

### 2.1 Materials

Polysulfone (PSf) polymer was purchased from Solvay Advanced Polymers (Alpharetta, GA) under the trade name of 'Udel Polysulfone P-3500 LCD'. The solvents for polysulfone membrane synthesis was dimethylacetamide (DMAc), tetrahydrofuran (THF), and ethanol, which were purchased from Sigma Aldrich. For ZIF-8 particles synthesis, zinc nitrate hexahydrate and 2-methyl imidazole supplied by Sigma Aldrich were used as reactants, and methanol was used as solvent. All chemicals were used as received without further purification. All gases (pure CO<sub>2</sub> and CH<sub>4</sub>) for the gas permeation testing were purchased from PT Samator, Indonesia.

### 2.2 Synthesis of ZIF-8 nanoparticles

ZIF-8 was prepared in-house in this work following the steps reported elsewhere (Cravillon *et al.* 2009). Briefly, 6.5 g of 2-methylimidazole was dissolved in 200 ml methanol and then mixed with a 200 ml of methanol solution containing 3 g of zinc nitrate hexahydrate. The mixture was vigorously stirred for one hour until it gradually turned cloudy. The suspension solution was then separated using a Beckman Avanti centrifuge for 15 minutes at 13,000 rpm, followed by another two cycles of re-suspension and centrifugation cycles with pure methanol to remove unreacted chemicals.

### 2.3. Fabrication of the Polysulfone-based dense mixed matrix membranes

The synthesis of pure polysulfone, as well as PSf-based MMMs, was conducted by solution blending and phase inversion techniques. PSf-based membranes were produced firstly by dissolving 22 wt.% of PSf in a mixture of DMAc, THF, and 14.4wt.% of ethanol. The solution was then mixed in a beaker glass using a magnetic stirrer at 60°C for 6 h to form a homogeneous casting solution. The solution was then casted on a glass plate with a casting knife at room temperature. The casted membranes were then soaked in water for 10 min and methanol for 2 h followed by drying (Julian *et al.* 2019).

### 2.4. ZIF-8 particles and membrane characterization

The characterization of the pure polymeric and mixed matrix membranes was conducted using Scanning Electron Microscope (SEM), Energy Dispersive X-Ray (EDX), Fourier Transform Infra-Red (FTIR), and X-Ray Diffraction (XRD) techniques. The surface morphology of the membranes was examined under Evo MA 10 Carl Zeiss SEM equipment with Pd/Au coating. The presence of Zn element as a representation of ZIF-8 and the quality of dispersion in the matrix of the membranes were examined with EDX connected to SEM analyzer. Chemical analysis

of the membranes was conducted using alpha FTIR. The crystallinity of the membranes was analyzed in a PANalytical Empyrean Thin-Film XRD device for 2 $\theta$  from 4 to 60° with 0.026° step size. ZIF-8 particles were analyzed using FEI Tecnai G2 20 TEM for imaging purposes.

### 2.5. The gas permeation test

The gas permeation performance of the dense mixed matrix membranes was tested in a stainless-steel flat sheet membrane permeation rig (effective area of 9.6 cm<sup>2</sup>). Prior to the gas permeation test, the thickness of the membrane was measured using a micrometre. The membranes in this work had a thickness between 50 to 60  $\mu$ m. All gas permeation tests were carried out at room temperature (around 30°C), and the volumetric flow rate of gas in permeate was measured by a bubble-flowmeter. For the hollow fibre composite membrane, a similar gas permeation rig was used and the permeate flow rate was recorded through a bubble-o-metre. The pure gas permeability was calculated according to equation (1) below:

$$P = \frac{Q}{\Delta p} \times l \quad (1)$$

where  $P$  is the gas permeability,  $Q$  is the permeate volumetric flow rate (ml.s<sup>-1</sup>),  $\Delta p$  is the pressure difference across the membrane (cmHg),  $A$  is membrane surface area (cm<sup>2</sup>), and  $l$  is membrane thickness (cm).

The ideal selectivity of membrane for a given gas pair was determined from the ratio of the permeability of fast gas (A) to slow gas (B) based on equation (2):

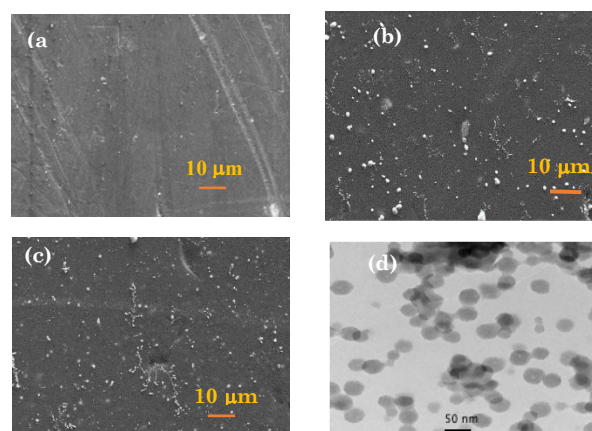
$$\alpha = \frac{P_A}{P_B} \quad (2)$$

### 3.1 The Morphology of Membranes

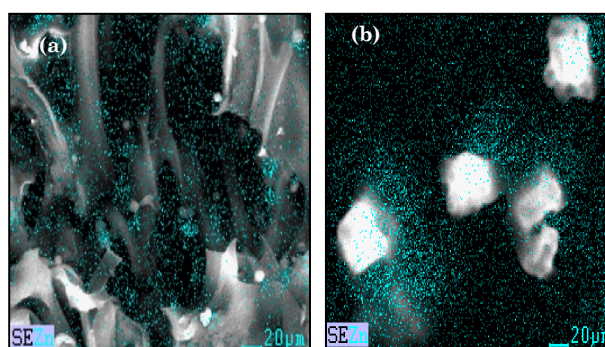
The structure of MMMs surface showed a rougher texture compared to pure polysulfone membrane. This was attributed to the presence of ZIF-8 particles inside the polymer matrix. The membranes were then analysed for their morphology using SEM and EDX. From the TEM analysis, ZIF-8 particles used in this study had particle size around 50 to 60 nanometres. ZIF-8 particles utilized as inorganic filler in MMMs were synthesized by room temperature reaction between zinc nitrate hexahydrate as the metallic component and 2-methyl imidazole as the organic ligand. The TEM image of as-synthesized ZIF-8 particles is depicted in Fig. 1d. The sample showed rhombic dodecahedron morphology. It is expected that the incorporation of nanoZIF-8 particles (size less than 100 nm), as well as the presence of the organic compound in ZIF-8, will provide better contact with polymer matrix in MMMs and avoid membrane defects.

The utilization of the nanometre size of ZIF-8 particles was intended to increase the dispersion of particles inside the polymer matrix. The dispersion of particles in this research was observed under SEM unit and also confirmed by EDAX spectra and Zn element mapping. The SEM analysis was conducted for the surface of pure polysulfone and polysulfone/ZIF-8-based MMMs

with 10 and 30wt. % loading of ZIF-8 particles. These MMMs were chosen to represent the low and relatively high particle loading in order to analyse the dispersibility of the particles inside the polysulfone matrix. From 1,000x magnification, it can be observed that the surface of pure polysulfone membrane (Fig. 1a) showed a relatively smooth surface. Fig. 1b and c depicted rough surfaces with white dots that might represent the presence of ZIF-8 particles. From the surface images of the membranes, the uniform distribution of ZIF-8 particles cannot be depicted directly. Further EDX analysis confirmed the occurrence of Zn element on the surface and also the uniformity of particles inside MMMs with 10 and 30wt. % of ZIF-8 as can be seen in Fig. 2. The presence of relatively big white particles did not really represent the Zn element; hence, we assumed that those might be attributed to the presence of contaminants during the casting process. In general, the EDX analysis did not only show the presence of ZIF-8 particles but also showed a relatively uniform distribution of particles inside the polymer matrix. From the comparison of EDX Zn element mapping between membranes with 10 and 30wt. % ZIF-8, it can be observed that membrane with 10wt. % ZIF-8 provided a more uniform Zn element distribution compared to the membrane with 30wt. % loading. At 30wt. % loading, ZIF-8 particles tend to agglomerate and could potentially alter the polymer matrix.



**Fig.1** SEM images of the surface of various membranes: (a) pristine polysulfone membrane, (b) MMM with 10wt. % of ZIF-8, and (c) MMM with 30wt. % of ZIF-8. (d) TEM image of ZIF-8 particles



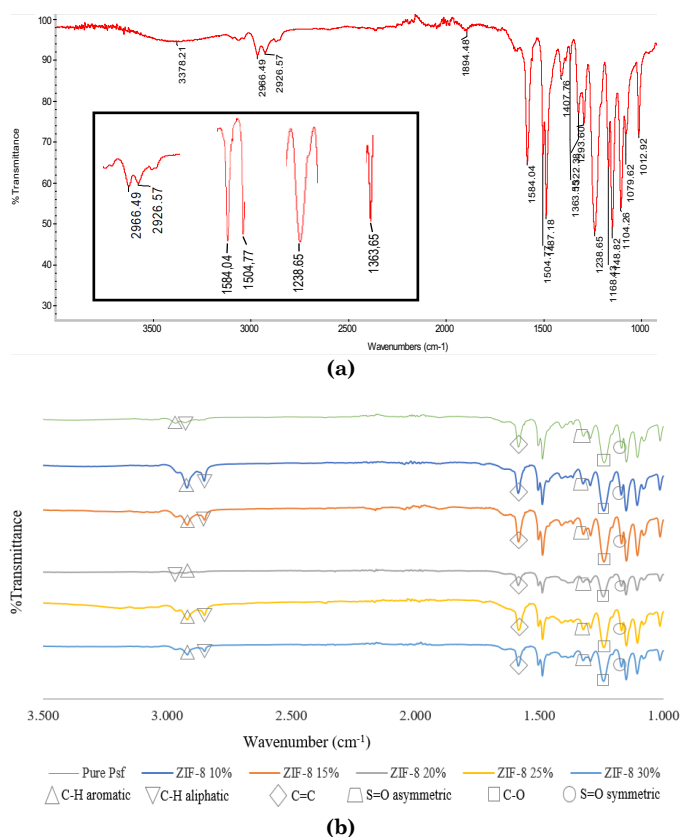
**Fig. 2** EDX mapping of Zn element on the surface of MMMs: (a) 10wt. % of ZIF-8 and (b) 30wt. % of ZIF-8



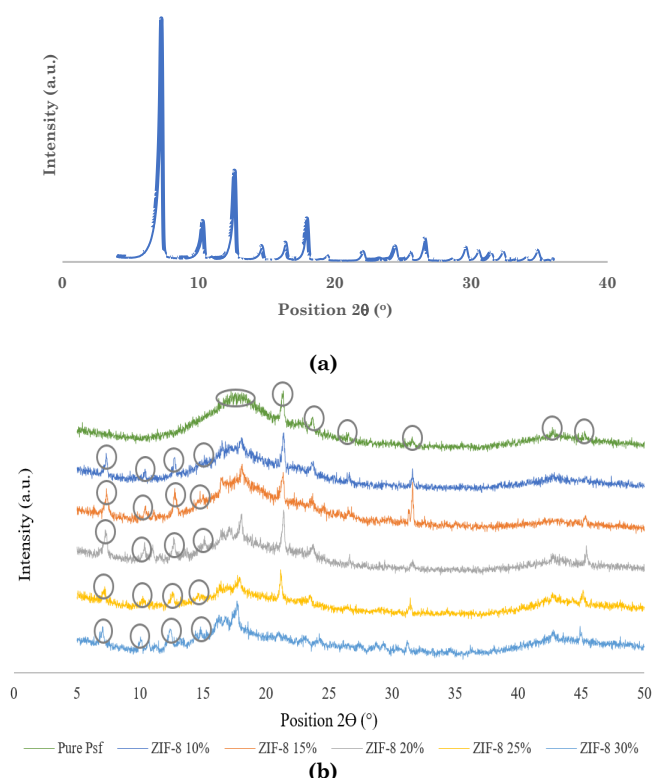
### 3.2. Chemical and Crystallinity Analysis of The Membranes

The chemical analysis of the membranes produced in this study was conducted using FTIR and the results are depicted in Fig. 3. The pure polysulfone membrane showed C=C bond at aromatic ring at 1504.77-1584.04 cm<sup>-1</sup>, C-H bond at aromatic and aliphatic rings at 2966.49 cm<sup>-1</sup>, and 2926.57 cm<sup>-1</sup>. The other bonds were C-O bond at ether at 1238.65 cm<sup>-1</sup>; asymmetric and symmetric S=O bonds at 1363.65 cm<sup>-1</sup> and 1168.43 cm<sup>-1</sup>. These results were in accordance with the results from another study (Ahn *et al.* 2008).

FTIR analysis of MMMs shown in Fig. 3b depicted a slight change in the position or wavenumber of some functional groups. These changes indicated an interaction between the ZIF-8 particles and the polysulfone matrix. The interaction might affect the separation performance of the resulting membranes as the interaction might form chemical bonding, such as hydrogen bond, that could potentially improve the mechanical performance of MMMs, especially at high pressure. However, to further analyze the formation of chemical bonds in MMMs from this study, further analysis needs to be conducted. In terms of peak intensity, the incorporation of ZIF-8 particles slightly affects the intensity of the peaks based on the percent loading of particles. However, there were no significant changes in peak intensity indicating the loadings used in this study were still low enough to change the structure of the polymer matrix (Sutrisna, *et al.* 2017, Sutrisna, *et al.* 2020b).



**Fig. 3** PFTIR spectra of various membranes : (a) pure polysulfone membrane and (b) MMMs with different ZIF-8 loading (wt. %)



**Fig.4** XRD patterns of (a) ZIF-8 particle and (b) various membranes

The change in the crystallinity of the membranes from this study was analyzed under XRD equipment. The XRD pattern of ZIF-8 particles is depicted in Fig. 4a. The crystalline nature of ZIF-8 particles was indicated by several peaks that was in accordance with previous study (Sutrisna, *et al.* 2017). In addition, the XRD patterns of pure polysulfone membrane and MMMs are presented in Fig. 4b. The XRD pattern of pure polysulfone membrane showed several peaks at 21.338°; 23.711°; 26.5199°; 31.6520°; 42.7712°; 45.3068° with an amorphous peak at around 17.5°. These signature peaks were in accordance with the previous study (Lonita *et al.* 2015 and Tran *et al.* 2020c). The incorporation of ZIF-8 particles added additional peaks of ZIF-8 for every type of MMMs, especially at 7.5°, 10.5°, 12°, 15°. All of these new peaks were the signature peaks of ZIF-8 particles. The inclusion of ZIF-8 particles at different weight percentages created a slight change in peaks intensity of the membranes. However, the difference in ZIF-8 peak intensity among membranes with different particle loading did not differ very much. This might be an indication that the polymer matrix still dominated the membrane matrix, hence the ZIF-8 peaks intensity for all membranes did not show much change.

### 3.3. Gas Separation Performances of The Membranes

The gas separation performances of the membranes produced in this study were tested using CO<sub>2</sub> and CH<sub>4</sub> pure gases as typical gases that constitute the biogas. The tests were conducted at room temperature and feed pressure of 1 bar. The gas permeability and selectivity of pure polysulfone and mixed matrix membranes were presented in Table 1.

**Table 1**

Pure gas separation performances of various ZIF-8/polysulfone-based membranes

ZIF-8 loading (wt. %)	CO <sub>2</sub> (Barrer)	CH <sub>4</sub> (Barrer)	CO <sub>2</sub> /CH <sub>4</sub>
0	17.1	0.77	22.2
10	20.3	0.86	23.4
15	21.4	0.87	24.5
20	22.8	1.00	22.6
25	24.5	1.14	21.5
30	26.3	1.24	21.2

The presence of ZIF-8 particles clearly increases the gas permeability through the membranes. ZIF-8 has pore diameter of around 3.4 Å that is suitable to separate CO<sub>2</sub> from CH<sub>4</sub>. The kinetic diameters of CO<sub>2</sub> and CH<sub>4</sub> are 3.4 and 3.8 Å, respectively. In addition, ZIF-8 has a relatively large surface area that improves its adsorption capacity to certain gas. However, the linker flexibility of ZIF-8 particles is also reported and it decreases its capability to discriminate gas mixture, especially gases that have a relatively close kinetic diameter, such as CO<sub>2</sub> and CH<sub>4</sub>. This was indicated by the decrease of CO<sub>2</sub>/CH<sub>4</sub> selectivity of ZIF-8-based MMMs in this study as can be seen in Table 1. In addition, the decrease of gas selectivity of the membranes was also attributed to the formation of micro voids during membrane synthesis. The micro voids inside the MMMs were mainly caused by the incompatibility between the particles and polymer matrix. Even though ZIF-8 has organic-linker, the aggregation of ZIF-8 particles was still possible in this study thus decrease the gas selectivity through the membranes. The other interesting phenomenon observed from Table 1 is the threshold loading of ZIF-8 in this study. The ZIF-8 loading of 15wt. % was observed and resulted in the maximum gas selectivity compared to the other membranes. It is an indication that further loading of particles resulted in particle aggregation or the formation of micro voids during membrane synthesis. Table 2 provides the gas separation performances of various mixed matrix membranes from different polymers and particles. The highest particle loading in this study was 30wt. %. Compared to other studies with 30wt. % ZIF-8, the CO<sub>2</sub> gas permeability and gas selectivity in this study were higher (Gholami *et al.* 2017).

However, compared to Matrimid-based membranes with NH<sub>2</sub>-UiO-66 particles, the gas permeability and selectivity in this study were relatively low. These were

attributed by the type of polymer used and the high CO<sub>2</sub> adsorption of NH<sub>2</sub>-UiO-66 particles (Anjum *et al.* 2015) as well as the high gas selectivity of Matrimid polymer (Rosdenas *et al.* 2015). Other study with the combination of MIL-101 and ZIF-8 particles inside polysulfone matrix showed a relatively similar gas permeability and selectivity compared to this study (Tanh Jeazet *et al.* 2017). Other studies using different particles inside polysulfone matrix showed a higher gas selectivity compared to this study due to the higher gas adsorption of NH<sub>2</sub> modified MIL-53 and graphene oxide-UiO-66 than ZIF-8 particles (Zornos *et al.* 2011 and Castarlenas *et al.* 2017). In addition, polysulfone-based mixed matrix membranes in previous studies showed comparable gas separation performances with this study in terms of gas permeability and selectivity (Guo *et al.* 2015). Hence, in general, the gas permeability of membranes from this study showed relatively higher CO<sub>2</sub> permeability than other membranes. In addition, the gas selectivity of membranes from this study presented comparable gas selectivity to other membranes. These indicate an opportunity for the membranes from this study to be developed for gas separation membranes.

#### 4. Conclusion

The mixed matrix membranes based on polysulfone and ZIF-8 particles were successfully synthesized in this study. Particle loading until 30wt. % was incorporated into the polymer matrix resulted in relatively uniform particle distribution. Morphological, chemical and crystallinity analysis suggested the interaction is not only physical but also chemical ways between the particles and polymer matrix. Gas separation performances of the membranes showed an increase in gas permeability with the increase of particle loading. The gas permeability of the membrane showed the highest value at particle loading of 30wt. %, and the gas selectivity showed a maximum value of 24.5 at particle loading of 15 wt. %. However, when particle loading higher than 15 wt%, the formation of micro voids attributed to the decrease in gas selectivity. The results from this study indicate the potentiality of polysulfone/ZIF-8-based mixed matrix membranes to be utilized in the biogas upgrading process.

**Table 2**

Gas separation performance of mixed matrix membranes from this study with previous studies

Type of particle	Particle loading (wt. %)	P <sub>CO<sub>2</sub></sub> (Barrer)	CO <sub>2</sub> /CH <sub>4</sub>	Ref.
NH <sub>2</sub> -UiO 66/Matrimid 9725	30	37.9	47.7	(Anjum <i>et al.</i> 2015)
Nanosheet Cu-BDC/Matrimid 5218	8.2	4.09	78.7	(Rosdenas <i>et al.</i> 2015)
NH <sub>2</sub> -MIL-125 (Ti)/Polysulfone	20	29.3	29.5	(Guo <i>et al.</i> 2015)
ZIF-8/Polyurethane	30	14.2	13.7	(Gholami <i>et al.</i> 2017)
NH <sub>2</sub> -MIL-53 (Al)/Polysulfone	25	3.3	65	(Zornoza <i>et al.</i> 2011)
MIL-101 (Cr) and ZIF-8/Polysulfone	24	24	25.8	(Tanh Jeazet, <i>et al.</i> 2016)
Graphite oxide-UiO-66/Polysulfone	24	14	45	(Castarlenas <i>et al.</i> 2017)
ZIF-8/Polysulfone	15	21.4	24.5	This study
ZIF-8/Polysulfone	30	26.3	21.2	This study

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