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Initiation of MOFs Hybrid Membrane Development for CO_2 Gas Separation

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Abstract. CO_2 gas separation technology is the main technology that determines the success of Carbon Capture, Utilization, and Storage (CCUS) activities, so it needs to continue to be developed in a more effective and efficient direction. Membranes are one of the promising alternative CO_2 separation technologies. Membrane technology can be developed using several materials, and what is currently being developed is Metal-Organic Frameworks (MOFs) because they have various advantages such as adjustable pore sizes and permanent properties. However, the cost of making MOFs material is still quite expensive, so further studies are needed.

In this study, research was conducted to develop a hybrid MOFs membrane using a mixture of MOFs and polymer materials. Polymers are relatively inexpensive materials and can be used to bind MOFs so that mixed-matrix membranes (MMMs) are obtained, where the polymer is the matrix material, and the MOFs are the filler material. The development of hybrid MOFs begins with the synthesis and characterization of several MOFs materials, namely Zr(BDC) and Zr(BDC-NH2) followed by the synthesis of hybrid MOFs using PSf polymer. The MOFs hybrid membrane sheets were then tested on a laboratory scale to determine their ability to separate CO_2 gas from CH4. Then a comparison was made between the CO_2 and CH_4 escape values from the pure polymer membrane and the MOFs hybrid membrane to determine the changes in permeability and selectivity that occurred.

The test results showed an increase in the flux value of CO_2 and CH_4 in hybrid MOFs, where the increase in passed CO_2 was far above that of passed CH_4, so it can be concluded that the addition of filler MOFs succeeded in increasing the permeability and selectivity of the membrane. With the increased permeability and selectivity, it is hoped that the MOFs hybrid membrane can be used as a choice for CO_2 separation technology in the future.

Keyword(s): *CO_2 separation, membrane CO_2 separation, MOF membrane, Polymer Membrane, CCUS*

1 Introduction

Research on CO_2 gas separation technology continues to grow along with the increasing awareness of environmental damage due to the effects of carbon gas on a large scale. One of the most popular programs to overcome this effect is through an activity called Carbon Capture, Utilization, and Storage (CCUS). CO_2 gas separation technology is one of the main technologies that will determine the success of these activities, so it needs to be continuously developed. In addition, CO_2 is a corrosive gas impurity, therefore it is necessary to reduce the levels of this gas to an acceptable level. Commonly used technologies for CO_2 separation include absorption processes, adsorption processes, cryogenics, and membranes.

The separation technique using the membrane method requires equipment that is relatively simple, compact, easy to control and operate, and easy to increase productivity [Stern, 1994]. Purification technology using membranes is relatively more profitable because it does not require phase transformation.

Currently, membrane technology can be optimal if it is used for natural gas purification with medium gas volume flows, but it cannot compete with amine absorption in large gas volume streams [Baker, 2004]. It is hoped that with better innovation in membrane technology, it will also compete for high-volume gas flows. This is catalyzed by the discovery of new porous materials called Metal-Organic Frameworks (MOFs) as an alternative and new perspective in membrane-based CO_2 gas separation technology. MOFs have potential because of their characteristics as porous materials and can be functionalized according to application requirements. MOFs are also easily composited with polymers to form membranes that can be applied as a CO_2 separation technology.

2 Study Literature

MOFs are porous crystalline materials formed through coordinate bonds between metal ion clusters as the center and organic ligands as a link that produces a framework [Furukawa et al., 2014]. The framework of MOFs is called secondary building units (SBUs) and has a permanent porosity [Rosi et al., 2005]. The uniqueness of MOFs includes large surface area, high thermal resistance, and modifiable structure. These properties make MOFs excellent candidates for application in various fields, including catalysts, adsorbents/gas separation, sensors, photoluminescence, fuel cells, batteries, and drug delivery. Prof. Omar Yaghi Laboratory at the University of California of Berkeley was a pioneer in discovering MOFs. Yaghi and Li synthesized metallic copper (Cu)-based MOFs using the hydrothermal method and had SBUs $Cu(4,4'\text{-}bpy)_{1.5}\cdot NO_3(H_2O)_{1.25}$ [Yaghi and Li, 1995]. MOFs have an adjustable structure that can produce different surface areas and pore sizes. The internal surface area of MOFs provides a potential high CO_2 adsorption capacity due to the efficient arrangement [Sumida et al., 2012].
Polymer membranes produce high selectivity, but the permeability is still relatively low [Yaghi et al., 2017]. Polysulfone is a polymer material that is often used in the manufacture of gas separation membranes and belongs to the glassy polymer group. Based on the literature [Jusoh et al., 2012], the permeability of CO_2 gas in the gas mixture decreases with increasing feed pressure. In another study, CO_2 gas permeability decreased and then increased after reaching the plasticization pressure, so pressure became one of the important parameters [Lock et al., 2018]. According to the Arrhenius equation [McKeen, 2017], the permeability will increase with increasing temperature. Both CH_4 and CO_2 gas have increased permeability with increasing temperature [Safari et al., 2009]. Based on the literature [Ettouney and Majeed, 1997], the permeability of CO_2 gas increases with the addition of CO_2 gas composition to the incoming gas mixture. In general, polysulfone (PSf) is a polymer composed of benzene which is para-substituted by sulfonyl and ether groups. PSf has a higher plasticization pressure (34 bar) when compared to other types of polymers such as polyimide (12 bar), bisphenol A polycarbonate (31 bar), and cellulose acetate (11 bar) [Bos et al., 1999]. Membranes with high plasticization pressure were able to maintain their selectivity under conditions of high pressure and CO_2 concentration compared to those with low plasticization pressure [Julian et al., 2012]. In addition, PSf also has high thermal resistance, mechanical strength, and wide pore size, making it suitable for use as a membrane in the CO_2 gas separation process [Anjum et al., 2020].
Polymer membranes generally have high selectivity, but the permeability is still low, so they are modified into Mix-Matrix Membranes (MMMs) or hybrid membranes. Zeolite is one of the materials used to produce MMMs membranes. Although the permeability has been improved, on the other hand, the selectivity of the zeolite MMMs membrane is still low. This is caused by the zeolite structure which is not easy to adjust or modify [Z. Kang et al., 2017].

Therefore, MOFs with easily regulated structures have the potential to increase the selectivity and permeability of polymers in CO_2 gas separation. Anjum and colleagues successfully modified zirconium-based MOFs with polyimide (PI) polymers. The MOFs hybrid membrane has a much higher selectivity and permeability when compared to the matrix polymer without filler, with an increase of up to 50% for selectivity and 540% for permeability. The thermal resistance is also higher than that of the pure polymer [M. W. Anjum et al., 2015].

The use of membrane technology to capture CO_2 is currently increasingly being used, for example in Indonesia, it is applied in Jambaran Tiung Biru, which began operating in 2022 with a capacity of 192 MMSCFD [Petroenergy.id, 2020]. Since 2000, membranes have been applied in Grissik to capture CO_2 combined with amine system technology with a capacity of 300 MMSCFD. The level of CO_2 in gas feed to the Grissik plant is around 30% while the output from the membrane is around 15% and eventually becomes 2% after passing through the amine system [Anderson, C. and Siahaan, A., 2005].

3 Methods

The successfully synthesized MOFs were blended with the polymer in the solution phase with a certain composition. The blending results are then molded to produce a hybrid MOFs membrane. The MOFs hybrid membrane is arranged in such a way on the gas permeation test equipment, to determine the rate of CO_2 gas permeation.

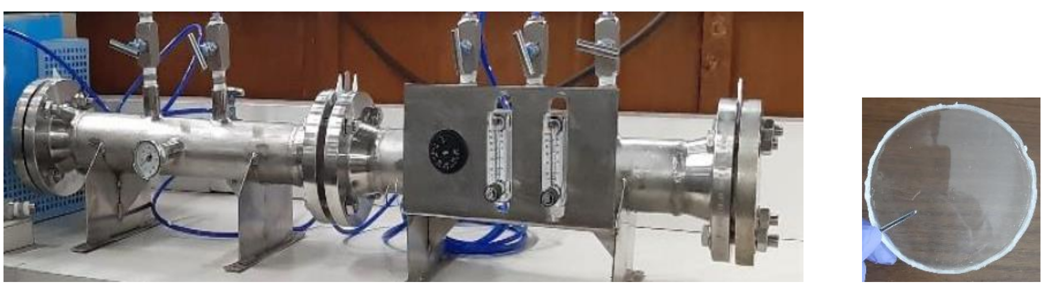
The following are the stages of the research method carried out:

1. Synthesis and Characterization of MOFs Materials.
2. Synthesis and Characterization of Hybrid MOFs Membranes.
3. Laboratory-scale Permeability Testing.

The MOFs that were synthesized in this paper are Zr(BDC) and Zr(BDC-NH2). The type of polymer used to make MOF hybrid membranes is Polysulfone (PSf).

Zr(BDC) was synthesized by the solvothermal method. $ZrCl_4$ was dissolved in DMF in a nitrogen atmosphere and sonicated, then H_2BDC and CH_3COOH were added. Zr(BDC-NH_2) type MOFs were synthesized by the same procedure, but the ligand was replaced with H_2BDC-NH_2. PSf polymer was dissolved in chloroform and stirred for several hours. The polymer solution was added with 3% and 5% MOFs, then sonicated and stirred. The mixture of PSf and MOFs was molded and evaporated slowly.

After that, the hybrid membrane test through a special tool in the laboratory. Parameters measured at the laboratory testing stage are as follows: the permeation of CO_2 and CH_4 with variations in pressure, gas flow rate, concentration, and temperature. **Figure 1** showed the arrangement of membrane testing.



(a) (b)

Figure 1. Laboratory Membrane Testing: (a) Special Tools to test Membrane; (b) Membrane Sample

4 Result and Discussion

BET Test Results and Pore Size of MOFs are shown in **Table 1**.

Table 1. The surface area of the sample vs reference

No	Sample / MOF types	Examination Result			Others Reference	
		Surface area (m^2/g)	Pore volume (m^3/g)	Pore diameter (A)	Surface area (m^2/g)	Ref.
1	Zr(BDC) 1	1118	0.54	15	1187	1
2	Zr(BDC) 2	1197	0.56	14	1187	1
3	Zr(BDC-NH_2) 1	341	0.27	23	956	2
4	Zr(BDC-NH_2) 1	587	0.37	19	956	2

[1]Cavka, et al, *J. Am. Chem. Soc.* **130** (2008) 13850. [2]Lee. et al. *ACS Appl. Mater Interfaces.* **9** (2017) 44847.

A comparison of sample BET test results compared with literature studies shows that the surface area characteristics are quite close for the Zr(BDC) material.

For other types of MoF, Zr(BDC-NH2), it is still quite different when compared to existing references. The possible cause is the activation process that is not appropriate yet. The activation process is crucial and significant to be able to take the remaining solvent that is trapped between the pores of the MOF material.

Tensile strength test results of MOF-Polymer hybrid membrane were shown in **Table 2**.

Table 2. Tensile strength of PSf Polymer vs MOF-Polymer hybrid membrane

No.	Membran	Komposisi MOFs (wt%)	Modulus Young (GPa)	Tensile Strength (MPa)
1	**PSf**	**0**	**0.7931**	**380.708**
2	PSf + Zr(BDC)	5	1.7244	551.817
3	PSf + Zr(BDC-$(OH)_2$)	5	0.8794	413.333

The tensile strength test proves that the addition of MOF to the polymer (hybrid membrane) could improve the mechanical properties compared to pure polymer (PSf), up to 45% for PSf + Zr(BDC).

CO_2 concentration trend on permeate side during permeation laboratory test of hybrid MOF/PSf membrane is shown in **Figure 2** below:

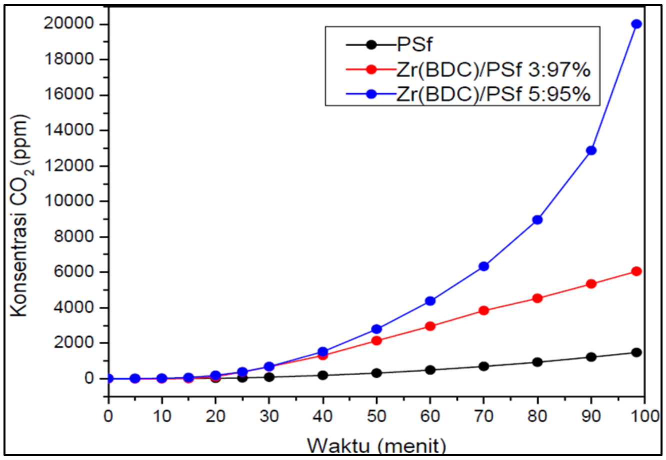


Figure 2. CO_2 concentration trend on the permeate side

The addition of MOF to the polymer (hybrid membrane) can increase the CO_2 permeation in the membrane compared to the pure polymer (PSf). Increasing the % weight of MOF on hybrid membranes (3% vs 5%) can increase CO_2 flux. Thus, the hybrid membrane has a higher CO_2 permeability than the polymer membrane.

The CO_2 permeability test on the hybrid membrane was carried out statically and dynamically. In the static test, the mixed feed gas flow (CO_2+N_2) is filled into the chamber membrane and maintained pressurized for some time, while in the dynamic test the feed gas continues to flow.

The dynamic system produces a higher passed CO_2 in permeate chamber than the static system, as shown in **Figure 3**.

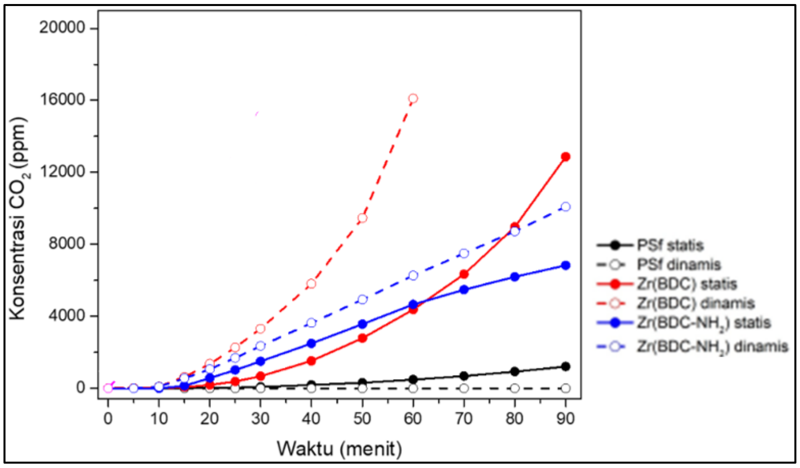


Figure 3. CO_2 concentration trend on the permeate side in static and dynamic test

The next step is testing the hybrid membrane using a mixed feed gas of CH_4 and CO_2 to determine the selectivity characteristics. The results of the CO_2/CH_4 separation test for polymer PSf and hybrid MOF membranes are shown in **Table 3**.

Table 3. Comparison of CO_2 and CH_4 concentrations in the permeate chamber

Waktu (menit)	Konsentrasi (ppm)					
	PSf		Zr(BDC)		Zr(BDC-NH$_2$)	
	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4
0	0	83	0	95	0	56
5	0	85	990	112	1028	68
10	20	88	3967	126	3732	75
15	238	91	9611	133	7853	80
18	428	92	20012	133	15356	82
20	554	93			20358	83

The test results showed an increase in the permeation of CO_2 and CH_4 in hybrid MOFs compared to polymer membrane, where the increase of CO_2 permeate was significantly higher than CH_4, this indicates that the addition of MOFs into the polymer (hybrid membrane) can increase CO_2 permeability as well as selectivity of CO_2/CH_4 gas. Based on this result, it was found that filler MOFs can increase permeability and selectivity to pure polymer membranes.

5 Conclusions

The research on the development of hybrid MOF membranes in this study is focused on the use of a mix of Zr(BDC) and Zr(BDC-NH_2) MOFs with PSf polymer. The study results showed an increase in the flux value of CO_2 and CH_4 in hybrid MOFs, where the increase in CO_2 flux was significantly higher than the CH_4. It is proven that the addition of filler MOFs can increase the permeability and selectivity of the polymer membrane which provides opportunities for the further development of hybrid MOFs membrane technology for CO_2 separation.

For more advantage, the mechanical properties test showed that the MOFs hybrid membrane had higher tensile strength than the pure polymer (PSf). Membrane Hybrid MOFs are expected to be able to compete with other CO_2 separation technologies.

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