



POLYSULFONE MEMBRANE WITH ZEOLITE FILLER FOR CO₂/CH₄ GAS SEPARATION: A REVIEW

¹Indri Susanti

1Department of Science Education, Faculty of Teacher Training and Education, Lamongan Islamic University. Jl. Veteran No.53A Lamongan, Indonesia

Email: indri_susanti@unisla.ac.id ; indrisusanti077@gmail.com

Article History

Received: 11 January

Revised: 25 February

Published: March 2019

Abstract

Membrane technology for gas separation applications are limited by a "trade-off" curve between permeability and selectivity. It show that permeability is high, selectivity obtained is low. This problem can be solved by preparation of Mixed-Matrix Membrane (MMMs) which can increase the value of permeability and selectivity. The MMMs with polysulfone polymers and zeolite fillers is more corresponding for gas separation. Addition of zeolite filler to polysulfone polymer in MMMs can improve the CO₂ separation performance. In this review, mechanism of gas separation in MMMs was carried out in the application of CO₂/CH₄ gas separation. In addition, the effect of addition, size and pore of zeolite filler in MMMs for binary gas separation were also discussed in this review.

Keywords: Mixed-Matrix Membrane (MMMs); CO₂/CH₄ Gas Separation; Polysulfone Polymer; Zeolite; Review.

How to cite: Susanti, Indri. (2019). POLYSULFONE MEMBRANE WITH ZEOLITE FILLER FOR CO₂/CH₄ GAS SEPARATION: A REVIEW. *Science Education and Application Journal (SEAJ)*. Vol. 1 No.1: 10-16.

I. INTRODUCTION (12pt)

Fossil fuels combustion produces components and contaminants such as CO₂, O₂, N₂, H₂O, and H₂S. Gas separation process should to be carried out for various applications later. The gas separation technology has been used is absorption technique using solvents such as polycarbonate and tributyl phosphate. However, the use of solvents in the gas separation process results contaminants which not environmentally friendly and require high costs [8].

In addition, the potential technology for gas separation and interesting to study is membrane technology. Membrane technology was applied to gas separation process until molecular level. Membrane technology has high efficiency and stability, more simple process, environmentally friendly, and low cost than other conventional processes [9]. Membranes are categorized into four types based on membrane material, that are: polymer membrane, inorganic membrane, liquid membrane, and mixed-matrix membrane (MMMs) [11]. However, the polymer membrane application is limited by performance of "Robeson trade-off line" curve between gas permeability and selectivity. The maximum performance of polymer membrane in gas separation at the "upper bound" which shows high selectivity and low permeability [11]. Inorganic membrane has high selectivity and thermal stability, but it has low permeability and sensitivity [11]. The efforts to develop membrane applications can be done with increasing the value of gas permeability and selectivity throught MMMs until reaches Robeson "upper bound".

Mixed-matrix membranes (MMMs) is a membrane consisting of a polymer and filler which can be composed by porous or non-porous inorganic material [9]. Some of the polymers has been used in MMMs are cellulose acetate, polyimid [8], Polyacetylene, poly-

dimethylsiloxane, poly-ethylsulfone ^[2], Polysulfone ^[15], and PVDF ^[19]. Polysulfone is a glass polymer that has adhesion between polymer-fillers. Polysulfone is better for MMMs preparation than elastic polymer ^[9]. In addition, polysulfone has good mechanical strength and thermal resistance ^[15].

The first porous material has been used as filler in MMMs is zeolite ^[9]. Zeolite is a aluminosilicate crystals which have a cage-like pore shape or framework with molecular size 0,5 – 1,2 nm [3,13]. Some zeolite type has been used as a filler in MMMs are zeolite-A ^[9], zeolite-X ^[14], Zeolite-Y ^[12], zeolite-T ^[15], ZSM-5 ^[5], and ZIF-8 ^[2]. In this article, a review was made of gas separation through mixed-matrix membrane (MMM) with polysulfone as polymer and zeolite as filler. Furthermore, this article also discuss about modification between polymer and zeolite, like the effect of adding zeolite and zeolite pore size in MMMs to CO₂/CH₄ gas separation.

II. MIXED-MATRIX MEMBRANE (MMMS)

MMMs is heterogeneous membrane consisting of inorganic filler which is affixed to a polymer matrix ^[7]. The schematic of MMMs with flat modules is shown in figure 1. The inorganic filler in MMMs aims to form a special permeation path by increasing selective permeability. Molecular sieving properties of inorganic filler added to the polymer matrix results increasing gas permeability on MMMs. Adapun preparation process of polymer matrix membrane with inorganic filler is efficient ^[7].

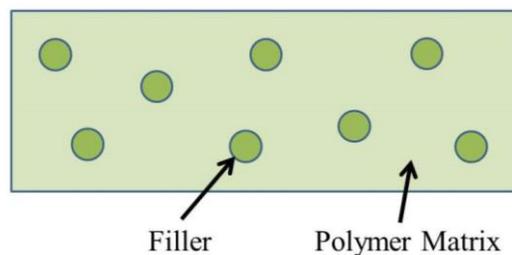


Figure 1. The schematic of MMMs with flat modules

MMMs with asymmetric hollow fiber modules have more effective membrane structure than flat modules. Hollow fiber membrane has a larger area per volume than flat module, good flexibility and simple preparation in module fabrication. Hollow fiber membrane has two layers that are widely applied due to some advantages, such as low material prices, easy synthesis process and better membrane performance than flat membrane ^[2]. The schematic of MMMs with hollow fiber modules is shown in figure 2.

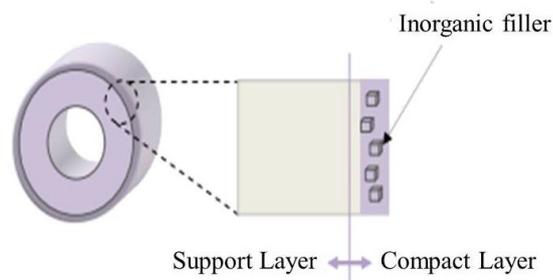


Figure 2. The schematic of MMMs with hollow fiber modules.

III. Selection of Polymer and Filler in Mixed-Matrix Membranes (MMMs) Preparation for Gas Separation

Selection of polymer and zeolite material is the important thing in Mixed-Matrix Membranes (MMMs) for gas separation. There are two types of polymer used in MMMs, that are glass polymer and rubbery polymer [2]. The rubbery polymer is more suitable for zeolite filler than glass polymer. However, it tends to push MMMs performance under “trade-off upper-bound” curve [11].

Some Polymers have been done in MMMs preparation are cellulose acetate, polyimide [8], Polysulfone [15], Polyacetylene, poly-ethylsulfone, poly-dimethylsiloxane [2], and PVDF [19]. Polysulfone is a glass polymer and hydrophobic that has adhesion between polymer-fillers. Polysulfone is better for MMMs preparation than elastic polymer [9]. In addition, polysulfone has good mechanical strength and thermal resistance [15]. The molecular sieving is important thing in the MMMs preparations for binary gas separation applications. The molecular sieving must be of the right size and has ability to distinguish gas molecules to be separated. Zeolite with three-dimensional network has a good diffusion path and it is corresponding for gas separation applications [2]. Zeolite is the first porous material as a filler in the MMMs preparations [9]. Zeolite is an aluminosilicate crystal which have a cage-like pore shape or framework with molecular size 0,5 – 1,2 nm [3,13]. Some zeolite type has been done as a filler in the MMMs are zeolite-A [9], zeolite-X [14], zeolite-Y [12], zeolite-T [15], ZSM-5 [5], and ZIF-8 [2].

IV. MMMs Applications for Gas Separation

Natural gas consumption has increased from year to year, i.e. 26,593 bcf (billion cubic feet) in 2014; 27,306 bcf in 2015, and 27,491 bcf in 2016 [17]. The composition of natural gas includes CH₄ gas as the main component of natural gas, CO₂, H₂S, H₂O, N₂, and hydrocarbon compounds such as ethane (C₂H₆), propane (C₃H₈), and butane (C₄H₁₀) [1]. The composition of natural gas with its concentration shown in Table 1. The presence of several components of natural gas causes the gas separation is needed, then used to various applications.

Table 1. The composition of natural gas [1]

Natural Gas Content	Concentration (Mole.%)
CH ₄	29.98 – 90.12
C ₂ H ₆	0.55 – 14.22
C ₃ H ₈	0.23 – 12.54
C ₄ H ₁₀	0.14 – 8.12
C ₅ H ₁₂	0.037 – 3.0
CO ₂	0.06 – 42.66
He	0.0 – 1.8
N ₂	0.21 – 26.10
H ₂ S	0.0 – 3.3

Based on the Table 1., CH₄ gas has the greatest concentration in natural gas. Then the greatest concentration after CH₄ gas is CO₂. Therefore, the CO₂/CH₄ gas separation is required then used for other applications. In the last 10 years, a number of membrane materials have been synthesized using polymers such as polyimide [8], intrinsic microporosity polymer (PIMs) [16], TR (thermal re-arranged) polymer [10], and applied on a laboratory scale for CO₂ gas separation from CH₄.

V. Mechanism for Binary Gas Separation in the MMMs with Polysulfone Polymer and Zeolite Filler

The mechanism of molecules transport in zeolite membrane begins with adsorption process of gas molecules on the surface of zeolite pore, then diffusion process around the surface of zeolite pore, and finally the desorption process to produce permeate ^[11]. Permeate is gas molecule has been separated from gas mixture in zeolite membrane (MMM).

Table 2. Physical Properties of CO₂, CH₄, N₂, O₂, and H₂ gas [2,23].

Physical Properties	Gas Molecule				
	CO ₂	CH ₄	N ₂	O ₂	H ₂
Molecular Weight (g/mole)	44.01	16.04	28.01	31.99	2.02
Kinetic Diameter (Å)	3.3	3.8	3.64	3.46	2.89
Critical Temperature (°C)	31	-82.1	-147.1	-118.6	-240.2
Critical Pressure (atm)	72.9	45.8	33.5	49.77	12.8
Critical Density (g/mL)	0.468	0.162	0.311	0.436	0.031

Gas adsorption process on the zeolite is a physisorption. The adsorption is exothermic and reversible ^[4]. Molecules are adsorbed into the zeolite pore due to the intermolecular interactions between adsorbent and adsorbate ^[2]. In this case the adsorbent is zeolite membrane (MMM) and the adsorbate is CO₂ gas. Adsorption of CO₂ gas on the zeolite is stronger than other gases such as H₂, CH₄ dan N₂. It causes of the dipole and quadrupole moments. The CO₂ molecule has dipole and quadrupole moments are higher than other gases ^[11]. The physical properties of several gas molecules are listed in Table 2.

Table 3. Structure Properties of Zeolites

Zeolite	Zeolite Type	Dimension Structure	Pore Size (Å)	Reference
4A	LTA	3D	3.8	[2]
5A	LTA	3D	4.3	[2]
X	Faujasit	3D	7.4	[21]
Y	Faujasite	3D	7.4	[21]
L	LTL	2D	7.1	[2]
ZSM-5	MFI	2D	5.6	[21]
ZSM-2	Faujasite	3D	5.7	[27]
SAPO-34	CHA	3D	3.8	[2]

Figure 3. The Schematic of Binary Gas Separation

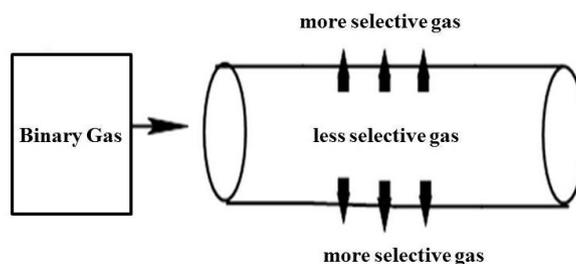


Figure 3 illustrate the process of binary gas separation. On the binary gas separation, selective gas in the MMMs will be diffused towards the outer layer and comes out as the permeate. Whereas, the less selective gas will be in the inner layer of membrane as a retentate.

VI. RESULT AND DISCUSSION

A. The Effect of Addition Zeolite Filler in MMMs for Gas Separation

The performance of MMMs is influenced by the number of zeolite filler added to polymer matrix. The increasing in the number of zeolite filler on polymer matrix can increase the value of permeability. The increasing the number of zeolites on polymer matrix cause the formation of an interface cavity that arises due to reduced adhesion between polymer and zeolite particle [5]. As shown in Table 4, addition of ZSM-5 filler with different amounts on polysulfone membranes showed different permeability value. Addition of ZSM-5 filler for 10% wt and 20% wt produces the permeability value of 2.0047 dan 2.2074 Barrer, respectively [5]. Nevertheless, in some other MMMs, the addition of zeolite filler decreases permeability value. [2].

B. The Effect of Zeolite Particle Size in MMMs for Gas Separation

The enhancement of zeolite particle size increase permeability value. The permeability value of Silicate-PDMS MMMs increases with increasing particle size of crystal silicate. The small zeolite particle size causes permeation process is difficult due to the number area of zeolite-polymer interface increased. It causes the mass transfer of molecule gas disturbed. However, the selectivity of MMMs in gas separation not affected by transformation of zeolite particle size [2].

C. The Effect of Zeolite Pore Size in MMMs for Gas Separation

Zeolite pore size also affects MMMs performance for gas separation. The larger zeolite pore size increases the MMMs performance in gas separation through the increasing permeability value. The large zeolite pore size reduces the occurrence of pore blockages in MMMs. In addition, gas molecules transport more easily pass through the larger zeolite pore and it causes the enhancement of permeability value [2]. However, the very large of zeolite pore size reduces selectivity value due to other gases also enter the zeolite pore. Therefore, selection of zeolite filler must be adjsuted between zeolite pore size and kinetic diameter of gas molecules to be separated.

Based on the Table 4., polysulfone membrane with zeolite-13X as a filler produces the larger permeability value than zeolite-A filler. It's corresponded with zeolites pore size are listed in Table 2 which show that zeolite-X pore size is larger than zeolite-A.

Table 4. Polysulfone Membrane with Zeolite Filler

Polymer / Filler	a	b	c	d	e	f	Reference
PSf/Zeolite-T	3	2	25	78.90	3.37	-	[15]
PSf/ Zeolite SAPO-34	10	3.48	25	314.02	28.2	-	[8]
PSf/ZSM-5	10	2 - 5	35	-	4.1351	2.0047	[5]
	20	2 - 5		-	2.3369	2.2074	
PSf/Zeolite-13X	10	7.8 atm	25	-	23.5	6.1	[14]
PSf –Ac/ Zeolite-3A	50	12	25	-	-	4.85	[9]
PSf/Zeolite-4A	-	2 atm	25	176 - 3720	1.6	-	[2]
PSf/ZIF-8	16	1	-	-	19.10	12.10	[2]
PSf / silica (rice husk)	40	-	-	-	33.31	8.46	[22]
Pure polysulfone	-	-	-	-	2.63	12.33	[15]

Explanation: a = Filler (% wt.); b = Pressure (bar); c = Temperature (°C); d = Permeation (GPU); e = CO₂/CH₄ Selectivity ; f = Permeability (Barrer).

VII. CONCLUSION AND SUGGESTION

Mixed-Matrix Membrane (MMMs) with zeolite filler corresponds to binary gas separation. MMMs with polysulfone polymer and zeolite filler increases the performance of gas separation due to the enhancement of permeability and selectivity value. Mixed-Matrix Membranes (MMMs) preparation with polysulfone polymer have been synthesized using zeolite-X filler. The further research in MMMs can be synthesized with zeolite-Y filler due to the zeolite-Y (7,4 Å) pore size similar with zeolite-X (7,4 Å). In addition, the pore size of zeolite-Y (7,4 Å) is larger than zeolite-A (3,8 Å) which can increase permeability value. It's due to the zeolite pore size enhancement can increase the value of permeability.

VIII. ACKNOWLEDGEMENT

Authors wish to thank to Universitas Islam Lamongan (UNISLA), East Java, Indonesia and the Ministry of Research, Technology and Higher Education of Indonesia for providing their facilities and helps for this article.

REFERENCES

- [1] Adewole, J.K., Ahmad, A.L., Ismail, S., Leo, C.P., Greenh, Int. J., (2013). *Gas Control*. 17. hal. 46 – 65.
- [2] Bastani, D., Esmaili, N., Asadollahi, M., (2013). "Polymeric mixed matrix membranes containing zeolites as a filler for gas separation applications: A review." *Journal of Industrial and Engineering Chemistry* 19. hal 375-393.
- [3] Chester, A. W. dan Derouane, E. G., (2009), "Zeolite Characterization dan Catalysis", Springer, New York Cheung O., Bacsik Z., Liu Q., Mace A. dan Hedin N., (2013), "Adsorption for CO₂ on highly selective zeolites NaKAdannano-NaKA", *Applied Energy*, **112**, hal. 1326–1336.
- [4] Dai, Z., Bai, L., Hval, K.N., Zhang, X., Zhang, S., Deng, L., (2016). *J. Membr, Sci. China Chem*. 497. hal.1-20.
- [5] Dorosti, F., Omidkhah, M.R., Pedram, M.Z., Moghadam, F., (2011). Fabrication and characterization of polysulfone/ polyimide-zeolite mixed matrix membrane for gas separation. *Chemical Engineering Journal* 171. hal 1469-1475.
- [6] Gong, H., Lee, S.S., Bae, T.H., (2017). "Mixed-matrix membranes containing inorganically surface-modified 5A zeolite for enhanced CO₂/CH₄ separation." *Microporous and Mesoporous Materials* 237. hal 82-89.
- [7] Ismail, A.F., Rahim, R.A., Rahman, W.A.W.A., (2008). *Separation and Purification Technology*. 63. 200.
- [8] Junaidi, M.U.M., Leo, C.P., Ahmad, A.L., Kamal, S.N.M., Chew, T.L., (2014). "Carbon dioxide separation using asymmetric polysulfone mixed matrix membranes incorporated with SAPO-34 zeolite." *Fuel Processing Technology* 118. hal 125-132.
- [9] Khan, A.L., Cano-Odena, A., Gutierrez, B., Minguillon, C., Vankelecom, Ivo F.J., (2010). "Hydrogen separation and purification using polysulfone acrylate-zeolite mixed matrix membranes." *Journal of membrane Science* 350. hal 340-346.
- [10] Kim, S., Lee, Y.M., (2015), *Prog. Polym. Sci.* 43. hal. 1-32.
- [11] Kosinov, N., Gascon, J., Kapteijn, F., Hensen, E.J.M., (2016). "Recent developments in zeolite membranes for gas separation." *Journal of Membrane Science* 499. hal 65-79.

- [12] Kusakabe, K., Kuroda, T., Murata, A., Morooka, S., (1997). "Formation of a Y-Type Zeolite Membrane on Porous α -Alumina Tube for Gas Separation". *Material and Interfaces Journal*. 36. hal. 649-65.
- [13] Langmi H. W., Walton A., Al-Mamouri M. M., Johnson S. R., Book D., Speight J. D., Edwards P. P., Gameson I., Danerson P. A. dan Harris I. R., (2003), "Hydrogen adsorption in zeolites A, X, Y dan RHO", *Journal of Alloys dan Compounds*, 356–357, hal. 710–715.
- [14] Mahmoudi, A., Namdari, M., Zargar, V., Khanbabaei, G., Asghari, M., (2014). "Nano composite PEBAX membranes: Effect of zeolite X filler on CO₂ permeation." *International Journal of Nano Dimension* 5(1). Hal 83-89.
- [15] Mohamad, M. Bt., Fong, Y.Y., Shariff, A., (2016). " Gas separation of carbon dioxide from methane using polysulfone membrane incorporated with zeolite-T". *Procedia Engineering* 148. hal 621-629.
- [16] McKeown, N.B., Budd, P.M., (2010). 1. hal. 63-68.
- [17] NOAA, (2017). "National Oceanic and Atmosphere Administration". [online]. Tersedia di <http://www.noaanews.noaa.gov/> [Diakses pada 7 September 2017].
- [18] Rezakazemi M, Amooghin A.E., Rahmawati-Montazer M.M., Ismail A.F., Matsuura. State-of-the-art membrane based CO₂ separation using mixed matrix membranes (MMMs): An overview on current status and future directions. *Progress in Polymer Science* 39 (2014) 817 – 861.
- [19] Shen, Y., Lua, A.C., (2012). "Preparation and characterization of mixed matrix membranes based on PVDF and three inorganic filler (fumed nonporous silica, zeolite 4A and mesoporous MCM-41) for gas separation." *Chemical Engineering Journal* 192. hal 201-210.
- [20] Vanherck, K., Koeckelberghs, G., Vankelecom, I.F.J., (2013). *Prog. Polym. Sci.* 38. (6). hal. 874-896.
- [21] Weitkamp, J., 2000. Zeolites and Catalysis. *Solid State Ionics*, 131, hal. 175-188.
- [22] Waheed, N., Mushtaq, A., Tabssum, S., Gilani, M.A., Ilyas, A., Ashraf, F., Jamal, Y., Bilad, M.R., Khan, A.U., Khan., A.L., (2016). "Mixed-Matrix Membrane Base on Polysulfon and Rice husk Extracted Silica for CO₂ Separation. *Separation and Purification Technology* 170. hal. 122-129.
- [23] Shekhawat, D., Luebke, D.R., Pennline, H.W., (2003). "A review of carbon dioxide selective membranes, A Topical Report", *National Energy Technology Laboratory United States Department of Energy*.