

Prospect of Oxyplus Hollow Fibre Membrane with Dense Polymethylpentene (PMP) Skin as Support-gutter Layer of Thin Film Composite (TFC) for Biogas Upgrading

Zulfida Mohamad Hafis Mohd Shafie,^{1,2} Abdul Latif Ahmad,^{1*} Sabine Rode,^{2**}
Bouchra Belaisaoui,² Denis Roizard² and Siew Chun Low¹

¹School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus,
14300, Nibong Tebal, Pulau Pinang, Malaysia

²Laboratoire Réactions et Génie des Procédés (LRGP) (UMR 7274),
Université de Lorraine / CNRS, ENSIC, 1, rue Grandville – BP 20451,
54001 Nancy Cedex, France

*Corresponding authors: chlatif@usm.my; sabine.rode@univ-lorraine.fr**

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ABSTRACT: *High selective polymers are bound to exhibit low intrinsic permeability. To mitigate this issue, thin film composite (TFC) membrane has been proposed whereby high selectivity, low permeability thin polymer layers are deposited on top of a thicker, highly permeable (even porous) materials. Nevertheless, deposition of thin film can be complicated on these structures due to limitation of fabrication methods (pore intrusion and support resistance to thin film solvent) and/or reduction of permeation efficiency (lateral diffusion). In this work, the potential of commercial Oxyplus® hollow fibre membrane as support-gutter layer was studied. Polymethylpentene (PMP), the material of the dense skin in Oxyplus has high gas permeability yet glassy enough to be self-standing, making it a possible candidate as a combined support-gutter layer. Ten fibres were potted together, assembled into a module, and tested in dead-end mode under 1–5 bar transmembrane pressure for CO₂, CH₄ and N₂ gases. The permeances were registered at 607.3 ± 31.3 GPU, 156.0 ± 13.1 GPU, and 84.6 ± 6.2 GPU, respectively, equivalent to a separation factor of 7.4 ± 0.4 (CO₂/N₂), 4.0 ± 0.2 (CO₂/CH₄) and 0.6 ± 0.1 (N₂/CH₄). With dense skin layer thickness of 0.1 ± 0.1 μm, these values are comparable to the PMP results in literatures and are suitable as support-gutter layer for low permeability polymers such as P84® polyimide.*

Keywords: Hollow fibre membrane, support-gutter layer, biogas upgrading, low permeability polymer, PMP skin

1. INTRODUCTION

Development of membrane gas separation processes for industrial purposes have been evolving tremendously in the last 50 years. Due to its low molecular size, industrial separation of gas by polymeric membranes has been monopolised by dense structures, except for certain specialised applications (e.g., uranium enrichment by Knudsen selectivity in the 1940s).¹ Nevertheless, researchers have found a correlation in the year 1991 (later updated in 2008) between gas permeability and its inverse relationship with selectivity across dense homogeneous polymers.^{2,3} Ever since then, various strategies have been proposed to overcome the low permeability of highly gas selective polymeric materials and make it economically attractive for membrane fabrication. One of them is to fabricate the dense layer of polymeric membranes as thin as possible without compromising its mechanical integrity. This can be achieved by anisotropic membranes (single material membranes with different structures across the cross section) or by composite structures (dense polymer deposited on top of microporous support of different material).

In both cases, the molecular separation and permeation performance of the membrane is highly regarded towards the dense skin while the mechanical viability of the membrane is regarded towards the porous support. Nevertheless, composite membranes such as thin film composite (TFC) have the added benefit for better control of the membrane layers to its specific functions, on top of allowing the use of more expensive materials (usually in the separating layer) in a thin, localised structure instead of being used for the whole membrane.⁴ Through the utilisation of TFC, higher permeance value can be achieved for highly selective, usually specialised polymer layer, which are normally grounded by its intrinsic physical limitation (reduction in diffusion coefficient with tighter molecular spacing) as explained by the Robeson upper bound limits.^{2,3} The increase in permeance are fundamental as noted in the volume flux equation for gas separation in dense membranes:¹

$$j_i = \frac{P_i(p_{io} - p_{il})}{\ell} \quad (1)$$

where j_i is the volume (molar) flux, P_i is the membrane's permeability which is a measure of the membrane's ability to permeate gas, P_{io} and P_{il} are the partial pressure of the gas component on either side of the membrane, and ℓ is the membrane thickness. The ratio of P_i and ℓ is called the membrane permeance. Hence, through this equation, reduction in membrane thickness would ideally increase the permeance and the permeate volume flux, reducing the areas needed to achieve a specific downstream capacity target of the separation unit.

For example, to achieve downstream permeate gas flowrate of 10 with $(P_{io} - P_{it}) = 1$, the reduction in selective layer thickness with $P_i = 10$ from 1 to 0.1 would increase the permeate flux and decrease the required membrane area by ten-fold without affecting the selectivity of the membrane. Note that in composite design, this equation would only govern the thin, dense selective layer. Hence, the increased overall thickness needed for mechanical stability which are mainly contributed by the porous substrate would not contribute to the reduction in gas flux. This is further enhanced when TFC is made in hollow fibre (HF) form, as it can give rise to modules of high specific surface (up to 10,000 m²/m³), which are very powerful tools for industrial gas treatment.

Despite the composite design advantages, there are several potential difficulties associated that need to be considered:

1. Lateral diffusion at the composite interface.^{4,6}
2. Impregnation of selective layer solution into the porous support.^{7,8}
3. Suitability of solvent used for selective layers with the underlying support.

The first two problems can be solved or minimised by proper control of surface pores of the support, introduction of a gutter layer in between the selective and support layer, or both. Meanwhile, the third problem needs experimental verification in terms of performance before and after treatment. Typically, polydimethylsiloxane (PDMS) has mainly been used as the gutter layer due to its high permeability, low selectivity characteristics.⁹ However, PDMS are rubbery polymers and are unsuitable for self-supporting purposes, requiring it to be supported on top of another porous layer. This creates the same problem related to the lateral diffusion explained, where impregnation of the PDMS solution can increase the gas permeation resistance across the membrane. Another high permeable polymer, polymethylpentene (PMP) has not been used as a gutter layer, despite its relatively high permeability of about 9.87 and 128 Barrer for N₂ and CO₂, respectively.¹⁰ Indeed, the value is below the permeability of PDMS, but PMP is advantageous as its high permeability yet glassy structure should allow it to be used as both support and gutter layer. Hence, to justify this, commercial anisotropic PMP-based HF membrane with dense outer layer, i.e. Oxyplus® by 3M was used for this approach to prepare TFC HF membrane, thanks to its good characteristics. Prospect from these base results will determine the feasibility of the samples as support-gutter layer for subsequent studies of TFC membrane fabrication for biogas separation.

2. EXPERIMENTAL

2.1 Module Preparation

Ten fibres of about 14 cm in length was bundled and prepared into a module. The fibres were cleaned with distilled water, potted together using Araldite® two-parts epoxy, and sealed on one end while attached into a Swagelok® connector on the other, as in Figure 1. All the fibres were used without prior modification or treatment, unless stated otherwise (drying at 60°C overnight and/or soak in N-methyl-2-pyrrolidone (NMP) for 3 h or 3 days to observe the stability of native HF).



Figure 1: Prepared fibre bundles.

2.2 Base Performance

The membrane module was fitted into a pilot unit (Figure 2) and tested with feed pressure of 1–5 bar gauge while permeating at atmospheric pressure. A flowmeter was used to determine the flowrate of the permeate gas. The testing was conducted at 35°C in dead end mode while the average last 10 data was taken as the final permeate flow rate when the permeate flow rate is stable for at least 1 h. N₂, CO₂ and CH₄ gas was used for this test, and the final value was averaged between the pressure difference and 8 test samples.

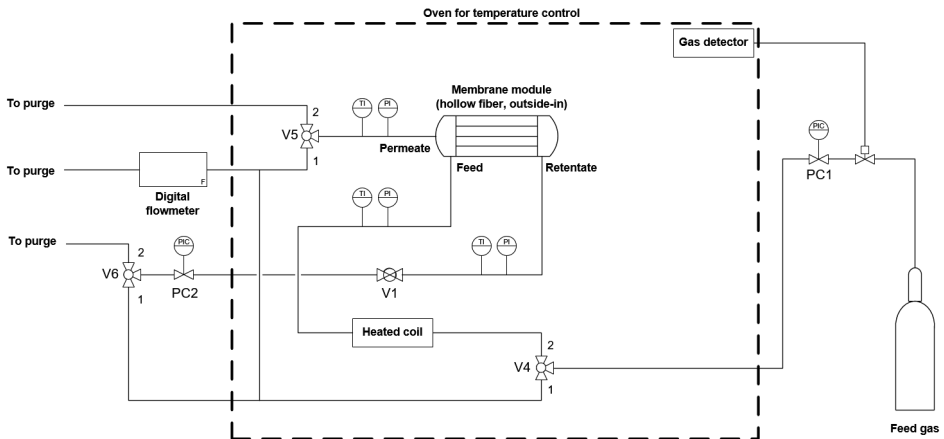


Figure 2: Test rig design used for gas permeation studies.

2.3 Influence of Testing Temperature

New membrane modules were tested at an increasing testing temperature of 25°C, 30°C and 35°C using N₂ gas. It is then cooled for 1 day and repeated at the same increasing testing temperature. Similar testing methodology was used as in Section 2.2. The final value was averaged between 3 test samples.

3. RESULTS AND DISCUSSION

3.1 Gas Permeation Base Performance

The membrane's base performance, calculated using Equation 1, is presented in Table 1. Permeance results suggested the suitability of this membrane as both support and gutter layer in terms of its separation performance, with permeance increment of CO₂ > CH₄ > N₂ and low CO₂/CH₄ selectivity, the main component of raw biogas. On the other hand, literature's permeability results suggested similar permeance values when back-calculated to get dense layer thickness of 0.1 ± 0.1 μm, suggesting the consistency of the permeance results of this commercial membrane with fabricated PMP membranes in literature.^{10–12} The N₂ permeance was also in the range reported in the data sheet of the supplier.¹³

Table 1: Base performance of Oxyplus HF.

Gas	Permeance (GPU)				Selectivity (this work)	
	Ref. 1 ¹⁰	Ref. 2 ¹²	Ref. 3 ¹¹	This work	N ₂	CH ₄
N ₂	99	67	54	84.6 ± 6.2	–	0.6 ± 0.1
CO ₂	1280	846	–	607.3 ± 31.3	7.4 ± 0.4	4.0 ± 0.2
CH ₄	–	149	121	156.0 ± 13.1	–	–

Notes: Permeances of the references were calculated by dividing the reported permeability with thickness of 0.1 μm

Nevertheless, it is worth to note on the higher permeance of CH₄ as compared to N₂. While N₂ is a minor component in raw biogas, its concentration can be quite high in landfill-sourced biogas.¹⁴ Depending on the gas feed's composition, this can reduce the purity of CH₄ in retentate, which is the gas of interest in biogas upgrading. It is, however, a minor consideration as majority of biogas sources do not have high concentration of N₂. On the other hand, majority of CH₄ is expected to be retained upstream by the selective layer, which will minimise the CH₄ loss in the permeate. Hence, the inverse N₂/CH₄ selectivity linked to the PMP gutter layer should not be a major concern.

3.2 Performance Stability at Different Test Temperature

Mechanical and performance stability of the self-supporting HF membrane may be compromised as PMP possess glass transition temperature, T_g at around 30°C–40°C.^{11,15} To elucidate this problem, the normalised permeance of N_2 between 25°C–35°C was recorded and presented in Figure 3. It was noted that the permeance was stable below 30°C but starts to degrade when tested above 30°C. This reduction was noted to be irreversible upon the second set of testing, where 12% of permeance loss was noted between 35°C (first test) and 25°C (second test). The permeance then increase with temperature for the second test, with final permeance loss of about 8% between 35°C (first test) and 35°C (second test). Despite of this, the reduction in permeance is still manageable as the base performance reported in Table 1 was conducted at 35°C.

Physical properties of polymer start to change when it reached its T_g . Hence, changes in permeance values were expected when the membrane was studied near this temperature. It is possible that the rearrangement of the polymer molecules near to the membrane surface caused the decrease in permeance, and later was fixed when the fibres were tested again (second test) at lower temperature. This is supported by the increased permeance during the second set of tests from 25°C to 35°C, although more studies need to be conducted to verify this claim.

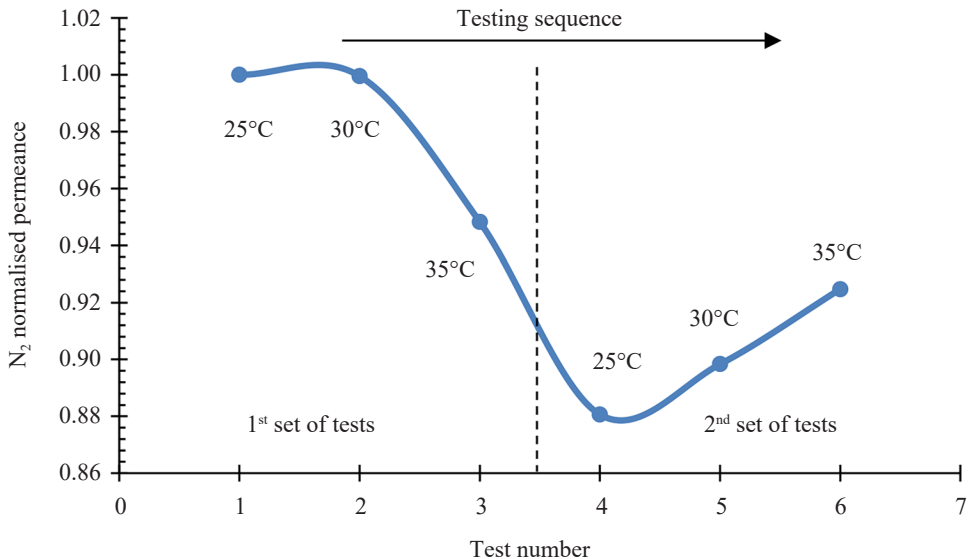


Figure 3: N_2 normalised permeances across the Oxyplus HF membranes at temperature range 25°C–35°C.

3.3 Permeance ratio between Oxyplus and Selective Layer (P84® PI)

In order to justify the suitability of the membrane as gutter layer with the selective layer, the permeance ratio (P_g/P_s), the ratio between the gutter's (P_g) and selective layer's permeance (P_s) was calculated.⁶ The ratio should be high so that permeance of the composites would be as near to the intrinsic permeance of the selective layer, maximising performance improvements in TFC.⁵ The permeability data from Hosseini et al. for P84® polyimide (PI) and the calculated P_g/P_s is given in Table 2, with assumption that about 0.1–0.5 μm thickness of P84 PI thin film can be coated onto the membrane.¹⁶ From the results, P_g/P_s was noted to be limited by CO_2 with the lowest permeance ratio of 44 for 0.1 μm P84 PI, which is in the practical range.^{5,6} While no details on P84 PI thickness below 1 μm was found, another commercial PI (Matrimid) has been reported with final coating thickness as low as 0.4 μm .¹⁷ Hence, it is safe to say that the P_g/P_s and the thickness assumption is in the achievable and positive range.

Table 2: Permeability data of P84 PI, expected permeance of P84 PI, and permeance ratio between Oxyplus and P84 PI (for 0.1 μm and 0.5 μm P84 PI thickness).

Gas	P84 permeability (Barrer) ¹⁶	P84 expected permeance (GPU), 0.1 μm	P_g/P_s , P84 = 0.1 μm	P84 expected permeance (GPU), 0.5 μm	P_g/P_s , P84 = 0.5 μm
N_2	0.050	0.50	169	0.10	846
CO_2	1.37	13.70	44	2.74	222
CH_4	0.028	0.28	557	0.06	2786

Notes: Expected permeance was calculated by dividing the permeability with the chosen thickness of the P84 layer

3.4 Performance Stability in NMP and at Drying Temperature

One potential problem with the fabrication of composite structures are the instability of the support polymers with the solvent and fabrication parameter of the dense selective layer. Hence, the membrane's permeance stability was tested versus drying temperature and solvent, i.e., NMP, a strong aprotic polar solvent used for P84 PI dissolution and coating for TFC fabrication. At 60°C, it was shown that the permeance decreased by only 11% for CO_2 and N_2 (Table 3). On the other hand, considering the harsh treatment applied to the HF, i.e., 3h (Table 4) and 3 days (Table 5) soaking in NMP, the HF appeared to be very stable with limited decrease of 5%–7% of CO_2 permeance. Meanwhile, N_2 & CH_4 permeance were highly increased, up to 83%–98% for N_2 . As a result, these permeances increment lead to decrease in selectivity values for CO_2 . However, this is not a dramatic issue

as in the complete TFC configuration, majority of CH_4 will be retained by P84 and only minimal concentration of CH_4 will become the feed for the support-gutter PMP layer.

Table 3 : Influence of heat treatment (60°C, 18 h) on the support layer's permeance and selectivity.

Gas	Permeance (GPU)		Differences (%)
	Base performance	After treatment	
N_2	80.3 ± 3.9	71.4 ± 4.9	-11.1
CO_2	563.0 ± 19.2	497.4 ± 25.2	-11.7
CH_4	132.2 ± 9.0	111.7 ± 5.1	-15.6

Gas pair	Selectivity		Differences (%)
	Base performance	After treatment	
CO_2/N_2	7.1 ± 0.3	7.1 ± 0.3	-0.5
CO_2/CH_4	4.3 ± 0.1	4.5 ± 0.1	3.1
N_2/CH_4	0.6 ± 0.1	0.6 ± 0.1	2.8

Table 4 : Influence of coating solvent (NMP) on the support layer's permeance and selectivity (3 h soak and dried at 60°C, 18 h).

Gas	Permeance (GPU)		Differences (%)
	Base performance	After treatment	
N_2	93.8 ± 5.4	185.8 ± 6.2	98.8
CO_2	768.1 ± 21.9	709.0 ± 23.3	-7.7
CH_4	195.3 ± 7.2	289.9 ± 7.2	48.4

Gas pair	Selectivity		Differences (%)
	Base performance	After treatment	
CO_2/N_2	8.2 ± 0.2	3.8 ± 0.1	-53.5
CO_2/CH_4	3.9 ± 0.1	2.4 ± 0.1	-37.9
N_2/CH_4	0.5 ± 0.1	0.6 ± 0.1	33.6

Table 5: Influence of coating solvent (NMP) on the support layer's permeance and selectivity (3 days soak and dried at 60°C, 18 h).

Gas	Permeance (GPU)		Differences (%)
	Base performance	After treatment	
N ₂	101.8 ± 3.8	187.2 ± 1.7	83.8
CO ₂	631.8 ± 9.7	597.7 ± 16.0	-5.4
CH ₄	195.1 ± 7.3	279.1 ± 7.7	43.0

Gas pair	Selectivity		
	Base performance	After treatment	Differences (%)
CO ₂ /N ₂	6.2 ± 0.2	3.2 ± 0.1	-48.6
CO ₂ /CH ₄	3.2 ± 0.1	2.1 ± 0.1	-34.0
N ₂ /CH ₄	0.5 ± 0.1	0.7 ± 0.1	28.6

4. CONCLUSION

The prospect of Oxyplus HF membrane as support-gutter layer for TFC membrane for biogas upgrading was elucidated. The sample suggested good base performance comparable to literature, and good P_g/P_s value with P84 PI. Some reduction in permeance was noted upon heat treatment, but negligible effects on the selectivity. Soaking the samples in NMP solvent changes the permeance and selectivity, but negligible differences were noted between 3 h and 3 days soaking period. Hence, as the targeted performance of the PMP dense layer was to retain a high permeance, it can be said that PMP is a promising candidate as support-gutter layer in the frame of TFC preparation with P84 PI.

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6. REFERENCES

1. Baker, R. W. (2004). *Membrane technology and applications*, 2nd ed. London: John Wiley & Sons.
2. Robeson, L. M. (2008). The upper bound revisited. *J. Membr. Sci.*, 320(1–2), 390–400, <https://doi.org/10.1016/j.memsci.2008.04.030>.
3. Robeson, L. M. (1991). Correlation of separation factor versus permeability for polymeric membranes. *J. Membr. Sci.*, 62(2), 165–185, [https://doi.org/10.1016/0376-7388\(91\)80060-J](https://doi.org/10.1016/0376-7388(91)80060-J).
4. Ghadimi, A. et al. (2018). Geometric restriction of microporous supports on gas permeance efficiency of thin film composite membranes. *J. Membr. Sci.*, 563, 643–654, <https://doi.org/10.1016/j.memsci.2018.06.025>.
5. Wijmans, J. G. & Hao, P. (2015). Influence of the porous support on diffusion in composite membranes. *J. Membr. Sci.*, 494, 78–85, <https://doi.org/10.1016/j.memsci.2015.07.047>.
6. Kattula, M. et al. (2015). Designing ultrathin film composite membranes: The impact of a gutter layer. *Sci. Rep.*, 5, 15016, <https://doi.org/10.1038/srep15016>.
7. Henis, J. M. S. & Tripodi, M. K. (1981). Composite hollow fiber membranes for gas separation: the resistance model approach. *J. Membr. Sci.*, 8(3), 233–246, [https://doi.org/10.1016/s0376-7388\(00\)82312-1](https://doi.org/10.1016/s0376-7388(00)82312-1).
8. Salih, A. A. M. et al. (2014). Interfacially polymerized polyetheramine thin film composite membranes with PDMS inter-layer for CO₂ separation. *J. Membr. Sci.*, 472, 110–118, <https://doi.org/10.1016/j.memsci.2014.08.025>.
9. Dai, Z., Ansaloni, L. & Deng, L. (2016). Recent advances in multi-layer composite polymeric membranes for CO₂ separation: A review. *Green Energy Environ.*, 1(2), 102–128, <https://doi.org/10.1016/j.gee.2016.08.001>.
10. Yasuda, H. & Rosengren, K. (1970). Isobaric measurement of gas permeability of polymers. *J. Appl. Polym. Sci.*, 14(11), 2839–2877, <https://doi.org/10.1002/app.1970.070141117>.
11. Roux, J. D. L. and Paul, D. R. (1992). Preparation of composite membranes by a spin coating process. *J. Membr. Sci.*, 74(3), 233–252, [https://doi.org/10.1016/0376-7388\(92\)80064-Q](https://doi.org/10.1016/0376-7388(92)80064-Q).
12. Mohr, J. M. & Paul, D. R. (1990). Effect of casting solvent on the permeability of poly(4-methyl-1-pentene). *Polym.*, 32(7), 1236–1243, [https://doi.org/10.1016/0032-3861\(91\)90227-A](https://doi.org/10.1016/0032-3861(91)90227-A).
13. 3M. (2019). Data sheet for 3M Membrana Oxyplus, capillary membrane, type PMP 90/200. Retrieved 25 January 2019 from https://www.membrana.com/healthcare/healthcare-data/documents/diapes%C2%AE/oxyplus%C2%AE-pmp-90-200/oxyplus_90_200.aspx.
14. Rasi, S., Veijanen, A. & Rintala, J. (2007). Trace compounds of biogas from different biogas production plants. *Energy*, 32(8), 1375–1380, <https://doi.org/10.1016/j.energy.2006.10.018>.
15. Lopez, L. C. & Wilkes, G. L. (1992). Synthesis, structure, and properties of poly(4-methyl-1-pentene). *J. Macromol. Sci. Polymer Rev.*, 32(3–4), 301–406, <https://doi.org/10.1080/15321799208021429>.

16. Hosseini, S. S. & Chung, T. S. (2009). Carbon membranes from blends of PBI and polyimides for N_2/CH_4 and CO_2/CH_4 separation and hydrogen purification. *J. Membr. Sci.*, 328(1–2), 174–185, <https://doi.org/10.1016/j.memsci.2008.12.005>.
17. Huang, Y. & Paul, D. R. (2007). Effect of film thickness on the gas-permeation characteristics of glassy polymer membranes. *Ind. Eng. Chem. Res.*, 46(8), 2342–2347, <https://doi.org/10.1021/ie0610804>.