# **PG&E GAS R&D AND INNOVATION**

# Membrane Separation Technical Analysis

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## 1 What is Membrane Separation

## 1.1 METHODOLOGY

Dissolution and diffusion into materials. A differential pressure across opposing sides of the film, provide for gas transport across the film (permeation). The rate of permeation is dependent upon the solubility coefficient and diffusion coefficient of the gas-membrane system. (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

In general, permeability measures the membrane productivity. Selectivity sets the purity of the recovered gas. It refers to the membranes ability to "select" particular molecules for passing through (e.g. CH<sub>4</sub>) and for preventing others from passing through (e.g. CO<sub>2</sub>). (Xia, 2018)

'Solution-diffusion' theory can be used to describe the mechanism of polymer membrane gas separations. Permeation consists of two steps: sorption and diffusion. Gas molecules are absorbed by the film based on chemical affinity. The sorbed gas molecules then can diffuse. Gas sorption are thermodynamically classified in two stages: condensation and mixing. The solubility coefficient depends on gas condensability and interactions between gas molecules and polymers. Diffusion coefficients depend on gas molecular sizes. Kinetic diameter  $(d_k)$  is widely used as the penetrant size for gas diffusion. For  $CH_4$ ,  $d_k$  is 0.38 nm, while the kinetic diameter of  $CO_2$  is 0.33 nm, which are very close to each other. (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

## Permeability (P), diffusion coefficient (D), and solubility coefficient (S)

(Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

 Von Wroblewski equation for pure gas which was based on steady-state empirical observations relating pressure and thickness for gas permeation rate

$$N = P\left(\frac{\Delta p}{l}\right) \tag{1}$$

where N is the permeation flux,  $\Delta p$  is the pressure difference across the membrane (p2 - p1 with p2 > p1), and I is membrane thickness. The proportionality coefficient (P) is called the permeability coefficient. It is assumed that a single gas goes through a polymer membrane of constant thickness (I) placed between two zones

Fick's first law for gas flux at steady state



$$N = \frac{C_2 - C_1}{l}D \tag{2}$$

where C1 and C2 are the downstream and upstream side gas concentrations of the polymer membrane respectively, and D represents the average effective diffusion coefficient.

Combining the above two equations yields

$$P = \frac{Nl}{P_2 - P_1} = \left(\frac{C_2 - C_1}{P_2 - P_1}\right)D$$
 (3)

• The gas equilibrium solubility coefficient is the ratio between gas concentration (gas molecules dissolved in the polymer at equilibrium) and the partial pressure of individual gas in the gas phase

$$S = C/P \tag{4}$$

Substitute equation (4) into (3) to get

$$P = DS (5)$$

The permeability coefficient (P) is determined by two elements: (1) a thermodynamic part which is the solubility coefficient (S) and determined by the number of gas molecules absorbed into and onto the polymer, and (2) a kinetic or mobility part which is the diffusion coefficient (D) determined by the mobility of gas molecules as they diffuse through the polymer. Permeability represents a pressure and thickness normalized gas flux (eqn (1)). It also determines the number of gas molecules dissolved and their flux through the polymer.

• Permeance (Q) is used to characterize asymmetric or composite membranes, while permeability is used for dense film. For industrial applications, a focus on permeance or flux instead of permeability should be made since one could make a very dense film and have high permeability, however permeance could be very low.



$$Q = \frac{P}{l} = \frac{N}{\Delta p} \tag{6}$$

## Selectivity $\alpha_{\scriptscriptstyle AB}$

(Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

Ideal selectivity

$$\alpha_{AB} = P_A/P_B \tag{7}$$

where PA and PB are the permeability coefficient of gases A and B, respectively. By default, the more permeable gas is taken as A, so that  $\alpha_{AB} > 1$ 

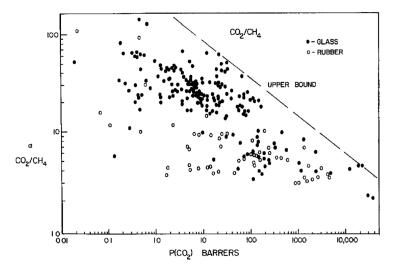


Figure 1 Literature data for CO2/CH4 ideal selectivity versus CO2 permeability (1991) (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

• When gas mixtures permeate across a membrane, the separation factor ( $\alpha^*_{AB}$ ), which represents the ability of a membrane to separate a binary gas mixture

$$\alpha_{\mathbf{A}\mathbf{B}}^* = (y_{\mathbf{A}}/y_{\mathbf{B}})(x_{\mathbf{A}}/x_{\mathbf{B}}) \tag{8}$$

where yA and yB are the mole fractions in the permeate, while xA and xB are the mole fractions in the feed

• Equation (8) can be rewritten



$$\alpha_{AB}^* = \alpha_{AB} \frac{p_2 - p_1 \left(\frac{y_A}{x_A}\right)}{p_2 - p_1 \left(\frac{y_B}{x_B}\right)} \tag{9}$$

The separation factor not only depends on the gaspolymer membrane system, but also on a driving force which is the pressure difference (p2 - p1) between upstream and downstream, as well as feed composition (xA, xB) and permeate gas (yA, yB)

When p2 is much higher than p1, eqn (9) simplifies

$$\alpha_{AB}^* = \alpha_{AB} \tag{9}$$

In summary, the process of permeation in a membrane can be broken down into two stages: sorption of gas molecules in the polymer and then diffusion of these molecules through the polymer film. Therefore, permeability P depends upon two factors: the solubility (S) and diffusion (D) coefficients. Gas separation selectivity depends upon the combination of these two factors.

#### 1.2 MATERIALS

There are polymer and mixed matrix membranes. Polymer membranes can be broken into 3 categories: co-polymer, cross-linked and blend. Inorganic membranes are made of metals, ceramics, zeolites or carbon molecular sieves (CMS). Mixed matrix membranes (MMM) consist of organic polymer combined with inorganic (or organic) particles.

Table 1 Organic polymers and inorganic membrane materials (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

Organic polymers	Inorganic materials
Polysulfone, polyethersulfone	Carbon molecular sieves
Cellulose acetate	Nanoporous carbon
Polyimide, polyetherimide	Zeolites
Polycarbonate (brominated)	Ultramicroporous amorphous silica
Polyphenylene oxide	Palladium alloys
Polymethylpentene	Mixed conducting perovskites
Polydimethylsiloxane	Metal organic frameworks (MOFs)
Polyvinyltrimethylsilane	



Polymer membranes have the two problems of permeability / selectivity trade-off (Robeson plots), and the effect of plasticization at high pressure or long-time period (because of  $CO_2$  or  $C_3$ <sup>+</sup> heavy hydrocarbons in biogas). Plasticization is an increase of polymer chains motion due to the presence of one or several molecules ( $CO_2$  or  $C_3$ <sup>+</sup> heavy hydrocarbons). This results in an increase in permeability and a decrease in selectivity.

Glassy polymer membranes have higher permselectivity, higher chemical resistance, as well as good thermal stability and mechanical strength compared to rubbery polymers. However, glassy polymers encounter plasticization effects at high pressure or long period of biogas upgrading.

Inorganic membranes have excellent thermal and chemical stabilities. Some have higher gas fluxes and selectivity (e.g. zeolites and CSM) relative to polymer membranes. Size and shape discrimination led to the narrow pore size distribution resulting in high selectivity.

MMM prepared with metal-organic frameworks (MOF) with polymers matrices are good for CO<sub>2</sub>/CH<sub>4</sub> gas separation. They have the potential for high selectivity, high permeability or both, compared to actual polymer and inorganic membranes. Transport properties of MMM are highly function of membrane morphology at the nano-scale, which is important for the overall membrane properties.

Table 2 Advantages and Disadvantages of inorganic membranes in comparison with polymeric membranes (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

Advantages of inorganic membranes	Disadvantages of inorganic membranes
Long-term stability at high temperatures	High capital costs
Resistance to harsh environments	Brittleness
Resistance to high pressure drops	Low membrane surface per module volume
Easy cleanability after fouling	Difficulty in achieving high selectivities in large scale microporous membranes
Easy catalytic activation	Generally low permeability of the highly selective (dense) membranes at medium temperatures
•	Difficult membrane-to-module sealing at high temperatures
	Low membrane surface per module volume

Membrane material selection depends on biogas composition.

- H<sub>2</sub>S rubbery polymer
- C<sub>3</sub><sup>+</sup> hydrocarbons silicone rubber
- H<sub>2</sub>O rubbery and glass polymers



- CO<sub>2</sub> polyimides
  - Matrimid®, Kapton®, P84 are inexpensive with low permeabilities
  - o 6FDA-based polyimides are expensive with better performance

## 1.3 MODULE TYPE

Three common types of configurations (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015):

- Hollow fiber module
- Spiral wound module
- Envelope (aka plate and frame) module

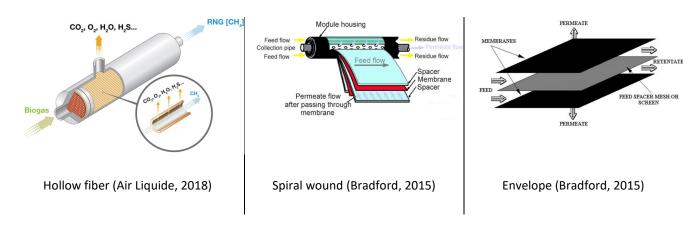


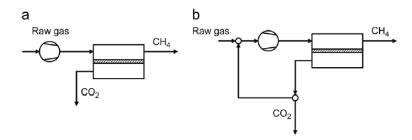
Table 3 Comparison of hollow fiber, spiral wound, and envelope (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

Property	Unit	Hollow fiber	Spiral wound	Envelope
Packing density Approximate area per module	$\frac{\text{m}^2 \text{ m}^{-3}}{\text{m}^2}$	<10 000 300-600	200–1000 20–40	30-500 5-20

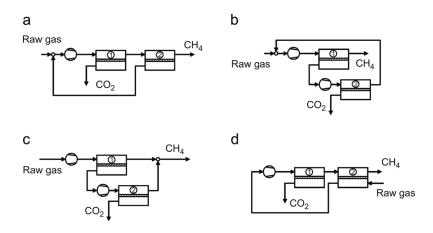
## 1.4 DESIGN OF MEMBRANE SYSTEMS FOR BIOGAS UPGRADING

Below are illustrations of various configurations for membrane only upgrading (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

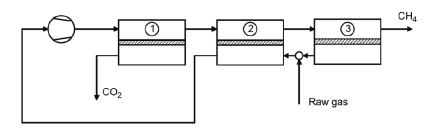




Single stage membrane-based biogas upgrading process using feed compression. Process (a) the permeate flows to the ambient. Process (b) the permeate is partially recycled to enhance the CH4 recovery.



Two stage processes for biogas upgrading





#### Three stage gas permeation process for biogas upgrading

Table 4 Various gas permeation upgrading processes are compared in terms of energy demand, CH4 recovery, required membrane area, and specific upgrading costs (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

Process	CH <sub>4</sub> recovery	Specific energy (kW h m <sup>-3</sup> )	Specific area (m² h m <sup>-3</sup> )	Upgrading costs (Euro ct h m <sup>-3</sup> )	Supply pressure (bar)
Single stage	0.855	0.277	1.70	0.228	20
Two stage (process (a))	0.957	0.318	1.92	0.220	20
Two stage (process (b))	0.997	0.286	1.69	0.201	20
Two stage (process (c))	0.973	0.295	1.57	0.206	20

Membrane biogas upgrading system design depends on location, biogas composition and other requirements. Using only a membrane separation process isn't ideal. Hybrid processes are more efficient: membrane separation technology combined with pressurized water scrubbing (PWS), amine swing absorption(AS), pressure swing adsorption (PSA), temperature swing adsorption (TSA), cryogenic separation, and a combined heat and power engine or multi-membrane separation stages. These configurations provide for lower costs.

Table 5 Comparison membrane area, methane losses and the cost items of membrane, gas absorption and hybrid process. (1 MM% = %106 USD) (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

Membrane area, methane losses and the cost items	Membrane process (stream A)	Membrane process (stream B)	Gas absorption process (stream A and B)	Hybrid process
Membrane area (10 <sup>2</sup> m <sup>2</sup> )	104.1	150.7	_	43.3
Methane losses (MM% per year)	1.137	1.431	0.144	0.983
Total capital investment (MM%)	2.836	3.688	6.226	4.196
Operating expenses (MM% per year)	1.033	1.318	2.853	1.516
Total separation cost (% per MSCF of feed)	0.244	0.311	0.373	0.296



Table 6 Comparison and evaluation of the costs of different biogas upgrading technologies (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

0 0	PSA techn	nology
9.0 >99.0	95.0-99.0 95.0-	99.0
99.96	98.0 80-99	9.5
0	4-7 4-7	
0.27	0.46 0.25-	0.43
m 70–80 °C High 120–160 °C		
Yes	Yes Yes	
ic solvent Amine solution	Activated carbon	
nazardous) (hazardous, corro	osive) (non-hazardous)	
50-100	85-115 50-10	05
Medium	High Low	
9500	10 400 7300-	-7600
5000	5400 4700-	-4900
3500	3700 3500-	-3700
14.4	12.8 10.8-	-15.8
11.2	9.2 6.5-1	
	99.96 0 0.27 Im 70–80 °C High 120–160 °C Yes ic solvent Amine solution (hazardous, correction) 0 50–100 Medium 9500 5000 3500 14.4 12.0	99.0

# 2 Membrane Separation Technologies

A comparison of commercial membrane suppliers is provided in the two tables below.

Table 7 Principal membrane suppliers for natural gas separation systems (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

Company	Principal natural gas separation	Membrane module type	Membrane material
Medal (Air Liquide)	$CO_2$	Hollow fiber	Polyimide
W.R. Grace	$CO_2$	Spiral-wound	Cellulose acetate
Separex (UOP)	$CO_2$	Spiral-wound	Cellulose acetate
Cynara (Natco)	$\overline{\mathrm{CO}_2}$	Hollow fiber	Cellulose acetate
ABB/MTR	CO <sub>2</sub> , N <sub>2</sub> , C <sub>3+</sub> hydrocarbons	Spiral-wound	Perfluoro polymers, silicon rubbers
Permea (Air Products)	Water	Hollow fiber	Polysulfone

**Table 8** Current commercial membrane materials and selectivities for separation of impurities from natural gas (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)



Component to be permeated	Category of preferred polymer material	Typical polymer used	Typical selectivities over methane $^a(\%)$
$CO_2$	Glassy	Cellulose acetate, polyimide, perfluoropolymer	10-20
H <sub>2</sub> S	Rubbery	Ether-amide block co-polymer	20-30
$N_2$	Glassy	Perfluoropolymer	2-3
	Rubbery	Silicone rubber	0.3
Water	Rubbery or glassy	Several	>200
C <sub>3+</sub> hydrocarbons	Rubbery	Silicone rubber	5-20

 $<sup>^{</sup>a}$  Selectivities are typical of those measured with high-pressure natural gas.



# 2.1 ADDITIONAL INFORMATION - PUBLICLY AVAILABLE BY VENDOR

## Air Products PRISM®

(Air Products, 2016)

High methane recovery configuration

		Raw biogas IN	Biomethane OUT	Vent
Composition				
Methane	mol%	55.0	98.0	0.3
Carbon Dioxide	mol%	45.0	2.0	99.7
Flow PB6050P3	nm³/hr	60.0	33.6	26.4
Flow PB4050P3	nm³/hr	23.0	13.0	10.0
Flow PB4030P3	nm³/hr	13.8	7.8	6.0
Pressure	barg	12.0	11.8	0.0

Power = 0.22 kW/nm³/hr raw biogas Methane recovery = 99.8%

## Low power configuration

		Raw biogas IN	Biomethane OUT	Vent
Composition				
Methane	mol%	55.0	98.0	0.3
Carbon Dioxide	mol%	45.0	2.0	99.7
Flow PB6050P3	nm³/hr	120.0	63.3	56.7
Flow PB4050P3	nm³/hr	46.4	24.4	21.9
Flow PB4030P3	nm³/hr	28.0	14.7	13.2
Pressure	barg	12.0	11.8	0.0

Power = 0.15 kW/nm³/hr raw biogas Methane recovery = 94%



### Low capital configuration

		Raw biogas IN	Biomethane OUT	Vent
Composition				
Methane	mol%	55.0	98.0	0.3
Carbon Dioxide	mol%	45.0	2.0	99.7
Flow PB6050N1	nm³/hr	350	176.8	173.2
Flow PB4050N1	nm³/hr	135.5	68.5	67.0
Flow PB4030N1	nm³/hr	81.6	41.2	40.4
Pressure	barg	12.0	11.8	0.0

Power = 0.17 kW/nm³/hr raw biogas Methane recovery = 90% Two stage system example

## **Bright Biomethane**

(Bright Biomethane, 2018)

- 99.5% methane recovery
- 0.22 kWh/Nm³ biogas electricity consumption
- No heat required for the biogas upgrading process
- Heat recovery > 0.25 kWt/Nm³ biogas covering the main energy consumption of the biogas facility.

A Bright Biomethane  $CO_2$  recovery unit can also be integrated with the standard 3 or 2 stage membrane upgrading systems. The high separation efficiency of the membranes means that the energy consumption of  $CO_2$  liquification is much lower than conventional systems.

No water or chemicals are needed in the Bright Biomethane process which means that there are no disposal problems, such as acid water or chemicals that can be an unforeseen cost with other technologies

Our systems are available from 40 Nm<sup>3</sup>/hr to 5,000 Nm<sup>3</sup>/hr (and higher).



## **Prodeval VALOPUR®**

(Prodeval Gas Process Engineering)

The process is based on the use of <u>SEPURAN®</u> highly efficient membranes (produced by EVONIK Company) that allows for a CH4 recovery > 99 %. After the biogas is pretreated, it is compressed between 10 and 16 barg, before entry into the membrane filtration modules.

	PERFORMANCE		
Flow treated	From 0 up to 100 % of the maximum flow		
Purification yield = CH <sub>4</sub> recovery yield	> 99,5 %		
Biomethane quality	B-type / H-type		
Availability of the upgrading unit	97 %		
Specific power consumption (kWhe/Nm³ of raw biogas to be treated)	0,22 < < 0,30		
Fatal heat recovery	yes		

#### **PRODUCT LINE**

	Flow (Nm³/h)	Maximum electrical power (kWe)	Heat recovery (water : 50°C - 60°C)	Dimensions
VALOPUR® 100	50 - 110	40	Studied case by case	20 feet container
VALOPUR® 200	100 - 220	80		W 6058 x L 2438 x H 2591 mm
VALOPUR® 300	200 - 330	120		
VALOPUR® 400	300 - 440	150		
VALOPUR® 500	400 - 550	190		40 feet container W 12190 x L 2438 x H 2591 mm
VALOPUR® 600	500 - 660	230		
VALOPUR® 700	600 - 770	260		
VALOPUR® 800	700 - 880	300		

VALOPUR® range enables to upgrade from 50 up to 880 Nm3/h of biogas as standard units. Higher flows are studied on demand.



# 3 R&D Opportunities

(Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

- Determine new materials with separation factor > 60, adequate permeance, suppression of plasticization at high CO<sub>2</sub> partial pressures, and enhanced long term stability of gas permeation systems
- Membrane-based biogas upgrading systems should simultaneously separate CO<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>S/CH<sub>4</sub> with membranes based on different types of materials
- Improve ease of operation and energy efficiency of membrane-based biogas upgrading systems



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