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

# Membrane Separation Technical Analysis

6/15/2018

Together, Building
a Better California

"The opinions, findings, and conclusions in the whitepaper are those of the authors and not necessarily those of PG&E. Publication and dissemination of the whitepaper by PG&E should not be considered an endorsement by PG&E, or the accuracy or validity of any opinions, findings, or conclusions expressed herein.

In publishing this whitepaper, PG&E makes no warranty or representation, expressed or implied, with respect to the accuracy, completeness, usefulness, or fitness for purpose of the information contained herein, or that the use of any information, method, process, or apparatus disclosed in this whitepaper may not infringe on privately owned rights. PG&E assumes no liability with respect to the use of, or for damages resulting from the use of, any information, method, process, or apparatus disclosed in this report. By accepting the whitepaper and utilizing it, you agree to waive any and all claims you may have, resulting from your voluntary use of the whitepaper, against PG&E."

# Table of Contents



# Table of Figures



# Table of Tables

# 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. $CH_4$) and for preventing others from passing through (e.g. $CO_2$). (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

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

  where N is the permeation flux, Δp is the pressure difference across the membrane (p2 - p1 with p2 > p1), and l 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 (l) placed between two zones

- Fick's first law for gas flux at steady state

$$N = \frac{C_2 - C_1}{l} D \qquad (2)$$

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

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

- 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

$$S = C/P \qquad (4)$$

- Substitute equation (4) into (3) to get

$$P = DS \qquad (5)$$

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.

$$Q = \frac{P}{l} = \frac{N}{\Delta p} \qquad (6)$$

## Selectivity $\alpha_{AB}$

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

- Ideal selectivity

$$\alpha_{AB} = P_A / P_B \qquad (7)$$

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 $\alpha_{AB} > 1$

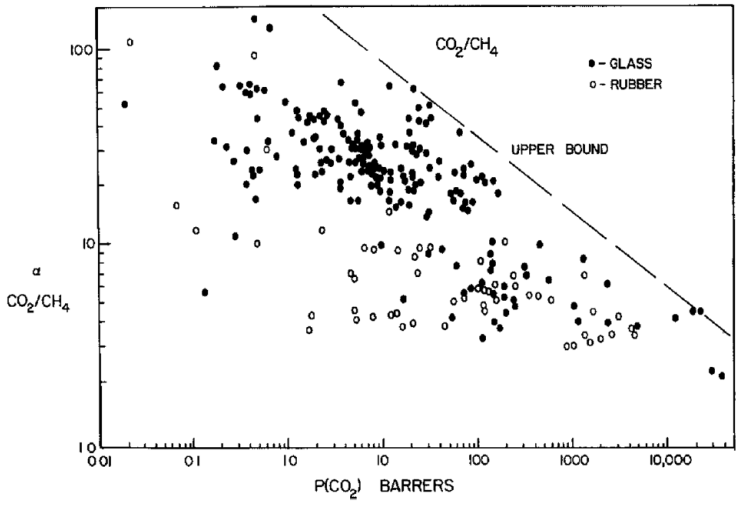



Figure 1 Literature data for CO2/CH4 ideal selectivity versus CO2 permeability (1991) (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)

- 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

$$\alpha^*_{AB} = (y_A / y_B)(x_A / x_B) \qquad (8)$$

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

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

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

$$\alpha^{*}_{AB} = \alpha_{AB} \qquad (9)$$

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 $C_3^+$ heavy hydrocarbons in biogas). Plasticization is an increase of polymer chains motion due to the presence of one or several molecules ($CO_2$ or $C_3^+$ 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 $CO_2/CH_4$ 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.

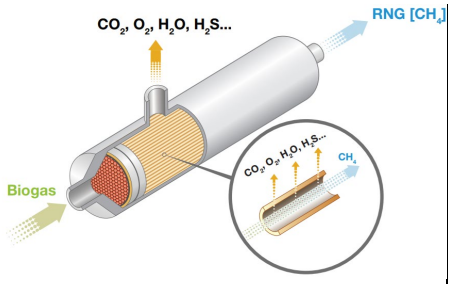
- $H_2S$ - rubbery polymer
- $C_3^+$ hydrocarbons - silicone rubber
- $H_2O$ - rubbery and glass polymers

- $CO_2$ – polyimides
    - Matrimid®, Kapton®, P84 are inexpensive with low permeabilities
    - 6FDA-based polyimides are expensive with better performance

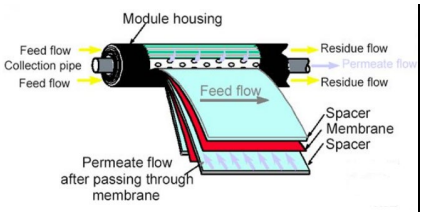
## 1.3 MODULE TYPE

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

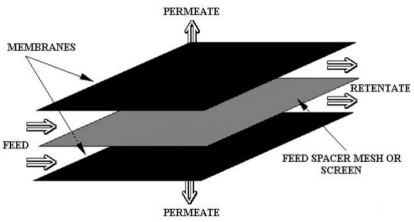
- Hollow fiber module
- Spiral wound module
- Envelope (aka plate and frame) module




Hollow fiber (Air Liquide, 2018)




Spiral wound (Bradford, 2015)



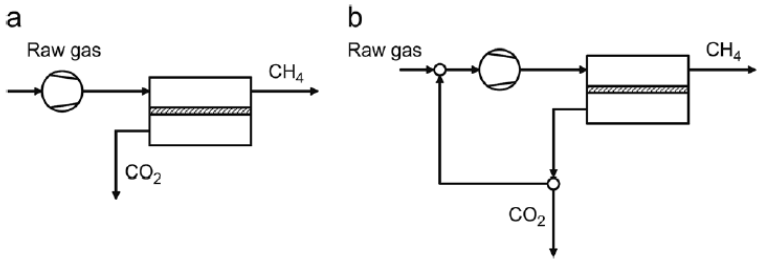

Envelope (Bradford, 2015)

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

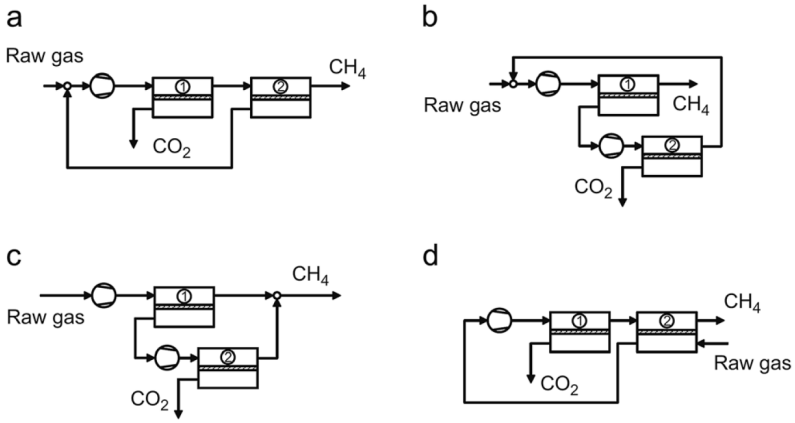
| Property | Unit | Hollow fiber | Spiral wound | Envelope |
|---|---|---|---|---|
| Packing density | $m^2\ m^{-3}$ | <10 000 | 200–1000 | 30–500 |
| Approximate area per module | $m^2$ | 300–600 | 20–40 | 5–20 |

## 1.4 DESIGN OF MEMBRANE SYSTEMS FOR BIOGAS UPGRADING

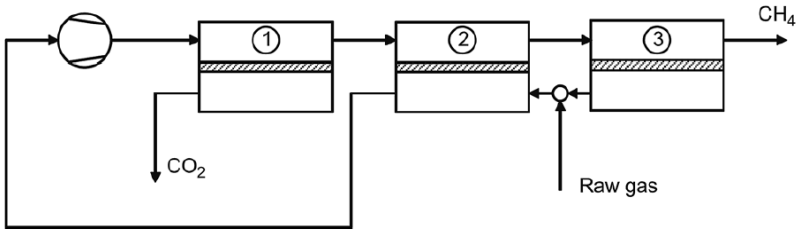
Below are illustrations of various configurations for membrane only upgrading (Chen, Ramirez, Kaliaguine, Vinh, & Rodrigue, 2015)




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 | $CH_4$ recovery | Specific energy (kW h $m^{-3}$) | Specific area ($m^2$ h $m^{-3}$) | Upgrading costs (Euro ct h $m^{-3}$) | 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 ($10^2$ $m^2$) | 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)

| Parameter | Water scrubbing | Organic physical scrubbing | Amine scrubbing | PSA | Membrane technology |
|---|---|---|---|---|---|
| Typical methane content in biomethane [vol%] | 95.0–99.0 | 95.0–99.0 | >99.0 | 95.0–99.0 | 95.0–99.0 |
| Methane recovery [%] | 98.0 | 96.0 | 99.96 | 98.0 | 80–99.5 |
| Typical delivery pressure [bar(g)] | 4–8 | 4–8 | 0 | 4–7 | 4–7 |
| Electric energy demand [kWhel $m^{-3}$ biomethane] | 0.46 | 0.49–0.67 | 0.27 | 0.46 | 0.25–0.43 |
| Heating demand and temperature level | — | Medium 70–80 °C | High 120–160 °C | — | — |
| Desulphurization requirements | Process dependent | Yes | Yes | Yes | Yes |
| Consumables demand | Antifouling agent, drying agent | Organic solvent (non-hazardous) | Amine solution (hazardous, corrosive) | Activated carbon (non-hazardous) | |
| Partial load range [%] | 50–100 | 50–100 | 50–100 | 85–115 | 50–105 |
| Number of reference plants | High | Low | Medium | High | Low |
| Typical investment costs [€/($m^3$ $h^{-1}$) biomethane] | | | | | |
| For 100 $m^3$ $h^{-1}$ biomethane | 10 100 | 9500 | 9500 | 10 400 | 7300–7600 |
| For 250 $m^3$ $h^{-1}$ biomethane | 5500 | 5000 | 5000 | 5400 | 4700–4900 |
| For 500 $m^3$ $h^{-1}$ biomethane | 3500 | 3500 | 3500 | 3700 | 3500–3700 |
| Typical operational costs [ct $m^3$ $h^{-1}$ biomethane] | | | | | |
| For 100 $m^3$ $h^{-1}$ biomethane | 14.0 | 13.8 | 14.4 | 12.8 | 10.8–15.8 |
| For 250 $m^3$ $h^{-1}$ biomethane | 10.3 | 10.2 | 12.0 | 10.1 | 7.7–11.6 |
| For 500 $m^3$ $h^{-1}$ biomethane | 9.1 | 9.0 | 11.2 | 9.2 | 6.5–10.1 |

# 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) | $CO_2$ | Hollow fiber | Cellulose acetate |
| ABB/MTR | $CO_2$, $N_2$, $C_{3+}$ 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 |
| $H_2S$ | 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 |
| $C_{3+}$ hydrocarbons | Rubbery | Silicone rubber | 5–20 |

[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** | $nm^3/hr$ | 60.0 | 33.6 | 26.4 |
| **Flow PB4050P3** | $nm^3/hr$ | 23.0 | 13.0 | 10.0 |
| **Flow PB4030P3** | $nm^3/hr$ | 13.8 | 7.8 | 6.0 |
| Pressure | barg | 12.0 | 11.8 | 0.0 |

Power = 0.22 $kW/nm^3/hr$ 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** | $nm^3/hr$ | 120.0 | 63.3 | 56.7 |
| **Flow PB4050P3** | $nm^3/hr$ | 46.4 | 24.4 | 21.9 |
| **Flow PB4030P3** | $nm^3/hr$ | 28.0 | 14.7 | 13.2 |
| Pressure | barg | 12.0 | 11.8 | 0.0 |

Power = 0.15 $kW/nm^3/hr$ 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** | $nm^3/hr$ | 350 | 176.8 | 173.2 |
| **Flow PB4050N1** | $nm^3/hr$ | 135.5 | 68.5 | 67.0 |
| **Flow PB4030N1** | $nm^3/hr$ | 81.6 | 41.2 | 40.4 |
| Pressure | barg | 12.0 | 11.8 | 0.0 |

Power = 0.17 $kW/nm^3/hr$ raw biogas
Methane recovery = 90%
Two stage system example

## Bright Biomethane

(Bright Biomethane, 2018)

- 99.5% methane recovery
- 0.22 $kWh/Nm^3$ biogas electricity consumption
- No heat required for the biogas upgrading process
- Heat recovery > 0.25 $kWt/Nm^3$ 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 $Nm^3/hr$ to 5,000 $Nm^3/hr$ (and higher).

## Prodeval VALOPUR®

(Prodeval Gas Process Engineering)

The process is based on the use of **SEPURAN®** 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 = $CH_4$ recovery yield | > 99,5 % |
| Biomethane quality | B-type / H-type |
| Availability of the upgrading unit | 97 % |
| Specific power consumption (kWhe/$Nm^3$ of raw biogas to be treated) | 0,22 < ... < 0,30 |
| Fatal heat recovery | yes |

**PRODUCT LINE**

| | Flow ($Nm^3/h$) | Maximum electrical power (kWe) | Heat recovery (water : 50°C - 60°C) | Dimensions |
|---|---|---|---|---|
| VALOPUR® 100 | 50 - 110 | 40 | Studied case by case | 20 feet container W 6058 x L 2438 x H 2591 mm |
| VALOPUR® 200 | 100 - 220 | 80 | | |
| VALOPUR® 300 | 200 - 330 | 120 | | 40 feet container W 12190 x L 2438 x H 2591 mm |
| VALOPUR® 400 | 300 - 440 | 150 | | |
| VALOPUR® 500 | 400 - 550 | 190 | | |
| 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 $CO_2$ partial pressures, and enhanced long term stability of gas permeation systems
- Membrane-based biogas upgrading systems should simultaneously separate $CO_2/CH_4$ and $H_2S/CH_4$ with membranes based on different types of materials
- Improve ease of operation and energy efficiency of membrane-based biogas upgrading systems

# References

Air Liquide. (2018). *Biogas Natural Energy Solutions.* Retrieved from Air Liquide: https://www.airliquideadvancedseparations.com/sites/medal/files/2018/05/01/biogas_customer.pdf

Air Products. (2016). *PRISM® Membrane Separators.* Retrieved from Air Products: https://membraneinsider.com/wp-content/uploads/2016/07/pb_biogas_brochure.pdf

Bradford, L. (2015). *Membrane Separation*. Retrieved from SlidePlayer: http://slideplayer.com/slide/4427966/

Bright Biomethane. (2018). *Membrane Biogas Upgrading Systems.* Retrieved from Bright Biomethane: https://www.brightbiomethane.com/wp-content/uploads/sites/2/2018/04/Bright-Biomethane-Brochure-EN-A-Bright-Idea-for-the-Perfect-Biogas-Plant-Solution.pdf

Chen, X. Y., Ramirez, A. A., Kaliaguine, S., Vinh, H. d., & Rodrigue, D. (2015, February). Membrane gas separation technologies for biogas upgrading. *RSC Advances, 5*(31). Retrieved from https://www.researchgate.net/publication/272423302_Membrane_gas_separation_technologies_for_biogas_upgrading

Prodeval Gas Process Engineering. (n.d.). *Valopur Biogas Upgrading Unit - Membrane Technology.* Retrieved from Prodeval: https://www.prodeval.eu/files/Telechargement/English/Fiche%20produit%20PRODEVAL_Valopur_EN.pdf

Xia, Y. (2018, January). Microporous Polymer Membranes for Gas Separation. Palo Alto, CA, USA: Stanford University.