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NOMENCLATURE

EU	European Union
PEBA	Polyether block amide
PA	Polyamides
PE	Polyether
PI	Polyimide
PSf	Polysulfone
PBT	Poly-butylene terephthalate
VOC	Volatile organic compound
TOC	Trance organic compounds
TSA	Thermal swing adsorption
PSA	Pressure swing adsorption
HF	Hollow fiber
MMM	Mixed-matrix membranes
FTM	Facilitated transport membranes
FSC	Fixed-site carrier
CMS	Carbon molecular sieve
HC	Hydrocarbons
CHFM	Carbon hollow fiber membranes
CNT	Carbon nanotubes
MOFs	Metal organic frameworks
PEG	Polyethylene glycol
PEO	Polyethylene oxide
LTA	Linde Type A
CHA	Chabazite zeolite
FAU	Faujasite zeolite
MOR	Mordenite zeolites
PVAm	Polyvinylamine
PSf	Polysulfone
NTNU	Norwegian University of Science and Technology



Ionic liquids	
Functional agent	
European Committee for Standardisation	
High quality gas	
Groningen quality as	
Low quality gas	
Transmissions system operators	
Distributions system operators	
Anaerobic digestion	
Intergovernmental Panel on Climate Change	
Carbon dioxide capture storage/utilization	
Direct air capture	
Monoethanolamine	
Low critical solution temperature	
Technical readiness level	
Industrial Technology Research Institute	
Membrane based carbon capture	
Membrane system engineering	
Polymers of intrinsic microporosity	
Thermal rearrangement (membranes)	
Polybenzoxazoles	
Nth-of-a-kind	



1 EXECUTIVE SUMMARY (3 pages max. all points)

1.1. Description of the deliverable content and purpose

One of the key-objectives of the BIOCOMEM project is the scale-up and manufacturing of advanced biobased materials for membrane production and their demonstration in CO_2 separation processes. This report, a deliverable from WP2, aims to gather information on the state-of-the-art membrane systems and membrane system configurations as well as the industrial requirements (material properties and manufacturing requirements) for three CO_2 separation applications: biogas, natural gas and post-combustion flue gas. For each application emphasis was given on cutting edge advances in membrane performance focusing on PEBA-based materials. The industrial requirements discussed in this report, along with other deliverables, will be taken into consideration for the module design activities for the bio-HF prototype membranes.

1.2. Brief description of the state of the art and the innovation brought

The advance of membrane technology is a subject undergoing intense study for the past years and the implementation of membranes in gas separation industry is undoubtedly gaining more ground. It is concluded that currently conventional technologies, such as amine-based absorption are still dominant in and gas and oil industry, however, the implementation of membranes is increasing.

With respect to membrane materials for CO_2 removal, polymeric membranes are still dominant in the market being commercialized for CO_2/CH_4 separation from gas streams, however, facilitated transport membranes and composites, such as mixed-matrix membranes show a good potential future applications. From all type of membrane module types, asymmetric hollow-fibers and spiral-wound are the ones preferred for large scale applications.

This state-of the art report also includes basic market information and current practices followed for the different gas separation applications with the goal to benchmark the bio-based PEBA membranes that will be fabricated within the BIOCOMEM project with the current practices and developments.

1.3. Deviation from objectives

N/A

1.4. If relevant: corrective actions

N/A

1.5. If relevant: Intellectual property rights

N/A



2 MEMBRANE GAS SEPARATION

Due to the world's large stock of low-cost fossil fuels, there is a strong requirement to explore opportunities for capturing CO_2 from (fossil fuel) combustion as a mitigation strategy to reduce the harmful emissions. Therefore, it is important to focus on the control of CO_2 and promote sustainable practice in all sectors. CO_2 separation from gas streams has been done using a variety of physical, chemical and biological technologies and methods. These technologies allow large-scale CO_2 separation in different industries including coal-fired power plants, refinery, and fertilizer industries. During the years, several techniques have been developed for CO_2 separation such as adsorption by liquid solvents, adsorption-absorption by solid materials, cryogenic distillation, calcium looping as well as membrane separation¹. A brief overview of these techniques can be seen in Table 1.

Method	Advantages	Disadvantages	Descriptions
Cryogenic distillation	Ability to operate in high volume Production of a product with a purity of more than 90% The ability to withstand high pressure	High operating costs High energy consumptions	This method is used in situations in which CO ₂ content higher than 50% in the gas mixture. At first, the gas mixture is liquefied and then the components are separated by distillation. Usually, in this method, four towers are used to separate carbon
Adsorption	Process simplicity The efficiency of this method is very high for light components (99.99% for hydrogen).	Often a batch process* Energy requirements comparable to membranes* Low Recycle A high volume of absorbent intake Desirable performance at low pressure	This method is based on the selective adsorption of a gas from the gas mixture on a solid adsorbent. The most important operating parameter of this process is pressure (80–800 psig) and typically takes place at temperatures of 30–60 °C. The adsorbent regeneration method depends on technical features and economic considerations
Absorption with amine	Simultaneous separation of different acid gases such as H ₂ S and CO ₂ Discovery of high purity products High removal rates can be achieved*	Operating pressure generally lower than membrane applications High thermal energy consumption for regeneration* Amines inactivation due to making chemical bonding with COS's, producing refractory materials Low efficiency of operating units Flow channelizing in contacting towers and foam formation due to the reactions of the amines	In this method, the separation of acid gases, such as CO_2 , is carried out by using aqueous solutions of alkanolamines through physical absorption. In this method, first carbon dioxide is absorbed in the amine solution, then the carbon dioxide-enriched amine is heated to release the absorbed gas and regenerates the amine. In this process, the absorption tower typically operates between 35–55 °C at high pressures (more than 2 atm), and the recovery tower often operates at atmospheric pressure or higher and temperatures in the range of 120–100 °C. These data can be modified and adjusted to increase absorption and recovery
Membrane separation	Low energy consumption Process simplicity Low space requirement No phase changing No need for chemical solvents Easy scale-up	Low capacity Poor thermal properties of the current commercially available membranes The trade-off between permeability and selectivity.	In this method, a thin film barrier material is used so that different species of the gas mixture have different transport velocities. The widely used membranes work based on the solution-diffusion mechanism. Membrane processes are very energy efficient and low-cost processes, but the current membranes suffer from the trade-off between the selectivity and the permeability for the permeants.

Table 1. CO₂ capture techniques advantages and disadvantages²

*These information were integrated according to DMT's experience and expertise.

¹ M. Bui *et al.*, "Carbon capture and storage (CCS): the way forward," *Energy Environ. Sci.*, vol. 11, no. 5, pp. 1062–1176, 2018. ² X. Chen, G. Liu and W. Jin, "Natural Gas Purification by Asymmetric Membranes: An Overview," Green Energy & Environment, 2020.



2.1 Membrane technology

Membrane-based gas separation has gained a great interest the past decades. It is becoming a competitive technology compared to conventional CO_2 removal technologies. Membranes are suitable to be applied in various environmental and energy processes, such as biogas upgrading, natural gas sweetening, CO_2 post-combustion capture (from flue gas), VOC recovery and hydrogen productions, potentially competing with some traditional separation methods in terms of energy requirements and economic costs. Specifically, membrane technology competes most directly against absorption for carbon dioxide removal³.

One of the key characteristics of membrane separation is that this technology requires no, or very little chemicals compared to standard unit operations. Membranes are also easy to scale up, energy efficient, and already widely used in various gas and liquid separation processes. For CO₂ capture/removal in particular, several types of membranes have been investigated, such as common polymers, microporous organic polymers, fixed-site-carrier membranes, mixed matrix membranes, carbon membranes as well as inorganic membranes³. Without a doubt, membranes have played an important role in gas separation during the last two decades and there is still a significant interest in further developing this technology.

Membranes are materials that form semi-permeable barriers and allow to pass certain type of chemical compounds through while other types of molecules are rejected. Depending on the desired separation different kind of membranes are selected for optimum results. Separation of chemical compounds by membranes is divided into six most common mechanisms: Knudsen diffusion, molecular sieving, solution-diffusion, surface diffusion, capillary condensation and facilitated transport^{4,5}.



Figure 1. Membrane separation technology in carbon capture

Most of the gas separation processes by membrane follow molecular sieving and solution-diffusion mechanisms. For any membrane, the separation process is described by three principal factors: permeability P, diffusion coefficient D and solubility S and the relationship is mathematically denoted as P=DS. P describes the flux through the membrane, D describes the mobility of the gas molecules within the membrane and S determines solubility of gas molecules in the membrane. Separation of ideal gas through membrane is driven by pressure difference between feed and permeate sides according to Fick's law⁴.

³ He, X.; Hägg, M.-B. Membranes for Environmentally Friendly Energy Processes. Membranes 2012, 2, 706-726.

⁴ A. A. Olajire, "CO2 capture and separation technologies for end-of-pipe applications: A review," Energy , vol. 35, pp. 2610-2628, 2010

⁵ Dai, Zhongde & Ansaloni, Luca & Deng, Liyuan. (2016). Recent advances in multi-layer composite polymeric membranes for CO2 separation: A review. Green Energy & Environment. 1.

Bio Co Mem

For any membrane, a parameter that determines its relevance is selectivity. To date, this parameter has been the major limiting factor in the membrane technology as typically other methods offer higher selectivity. However, membrane-based separation benefits from its simplicity, the absence of waste streams and the fact that the process does not require energy regeneration. Moreover, membranes can be implemented in chemical reactors thereby integrating reaction and separation processes.

2.2 Membrane module types

According to many reports, there are typically six types of membrane modules used in gas separations at present, including plate-and-frame modules, spiral wound modules, tubular modules, hollow fiber modules, and rotating disk modules. When membrane gas separation is applied, a large surface area is required for high process capacity. Nowadays, hollow fiber, spiral wound and envelope type modules are three common types of configuration used for industrial applications.

An important indicator to evaluate a membrane module is the packing density which equates to the surface area of membrane per volume inside the module⁶. Hollow fiber module generally has the highest packing density (Table 2) where the module consists of a cylindrical vessel that is filled with bundled strands of hollow fibers. Another type of module used in post-combustion application is the envelope type, in which the envelopes or discs are stacked layer by layer with a permeate pipe through the centers. The packing density usually lies within the range of 300-1000 m²/m³⁷. Since the surface area of the envelope has lower packing density, lower surface per module and higher cost for module requirement, commonly used membranes are hollow fiber and spiral wound modules⁸.

Module type	Unit	Spiral Wound	Hollow Fiber	Envelope
Packing Density	m^2/m^3	100-1000	<10000	200-500
Pressure drop		High and longer permeate	High in the fibers	Moderate
Cleaning		Hard	Chemical washing or replacement	Medium
Manufacturing		Easy and Cheap	Cheap	Easy
Approximate area per module	m ²	20-40	300-600	5-20
Cost for module	€/m ²	8-37	2-8	45-175

Table 2.	Comparison	of membrane	modules ^{8,9,10}
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In order to meet different industrial and domestic demands, different membrane arrangements are formulated; thus, various casting techniques have been implemented to obtain different types of the membrane configuration such as flat sheet membrane (casting), hollow fibre membrane (spinning), and composite membrane (dip coating)¹¹. Table 3 lists the commercial suppliers involved in biogas separation, most of them using hollow fibre membrane configuration.

⁶ Z. Wang et al., CO2-selective membranes: How easy is their moving from laboratory to industrial scale? Elsevier Inc., 2018. ⁷ M. Mulder, "Basic principles of membrane technology," 1991.

⁸ Chen, X. Y., Vinh-Thang, H., Ramirez, A. A., Rodrigue, D., & Kaliaguine, S. (2015). Membrane gas separation technologies for biogas upgrading. RSC Advances, 5(31), 24399–24448.

⁹ "https://www.borsig.de/uploads/tx_bcpageflip/BORSIG_Membrane_Technology_GmbH_E.pdf."

¹⁰ Y. Wang, L. Zhao, A. Otto, M. Robinius, and D. Stolten, "A Review of Post-combustion CO2 Capture Technologies from Coal-fired Power Plants," Energy Procedia, vol. 114, no. November 2016, pp. 650–665, 2017.

¹¹ B. Ladewig, M. Nadhim and Z. Al-Shaeli., Fundamentals of Membrane Bioreactors. Materials, Systems and Membrane Fouling., Singapore: Springer Transactions in Civil and Environmental Engineering, 2017.

Supplier	Module type	Polymer
Air Liquide Medal	Hollow fibre	Polyimide, polyaramide
Air Products	Hollow fibre	Polysulfone
GMT Membrantecnik	Envelope	Poly (ethylene oxide) poly (butylene terephthalate)
Evonik	Hollow fibre	Polyimide
IGS Generon Membrane Technology	Hollow fibre	Tetrabrome polycarbonate
Airrane	Hollow fibre	Polyimide
MTR Inc.	Spiral wound	Perfluoro polymer, silicon rubber
Parker	Hollow fibre	Polyphenylene oxide
Praxair (no longer active)	Hollow fibre	Polyimide
UBE Membranes	Hollow fibre	Polyimide
UOP Former Grace	Spiral wound	Cellulose acetate

Polymeric membranes specifically are attractive because they can be manufactured into units with very high surface areas, either in the form of hollow fibers arranged in the shell and tube configuration (85% of the market) or in the form of flat sheets packaged as thin film or spiral-wound modules, with less area but more resilience against adverse conditions¹².

2.2.1 Flat sheet film

Flat sheet membrane is a relatively simple method used to fabricate/prepare membranes and is widely used at laboratory scale. In industrial scale, the casting method employed is usually, in contrast with the laboratory, a continuous mode, where the molecular weight, concentration of the polymer and the kind of solvent used are the three more controlled factors determining the performance. In this case, the casting thickness can roughly vary from 50 to 500 μ m. Polymer solutions can be easily prepared and cast directly to a thin film either from a homogenous polymer solution using one of the supporting layer or polymer films with coating layers adjusting the thickness of the membranes¹¹.



Figure 2. Schematic of a spiral-wound membrane

In summary, flat sheet membranes are relatively straightforward to prepare, as they are very effective for characterising on laboratory scale, Nonetheless, higher surface area per volume unit such as hollow fiber or spiral wound are required in industrial scale¹¹.

¹² A. D and e. al., "State-of-the-art Adsorption and Membrane Separation Processes for Carbon Dioxide Production from Carbon Dioxide Emitting Industries," Separation Science and, vol. 44, p. 1273–1421, 2012.



2.2.2 Spiral-wound

Spiral-wound membrane configurations allows for a large membrane area in a low-volume module. These developments are certainly not trivial and require the membrane to be cast on a support, and to be flexible, strong and easy to handle.

Figure 3 shows an example of spiral wound module unit for CO_2 separation applications. It consists of several membrane envelopes, which wound around a perforated central collection tube together with spacers. Then module units are placed inside a tubular pressure vessel. Generally, a typical industrial-scale spiral wound module contains one tubular pressure vessel and several module units. The spacers are used not only to keep the distance between the membranes but also to enhance the mass transfer at a minimum pressure drop. Feed passes axially down the module across the membrane envelope and a portion permeates into the membrane envelope, where it spirals toward the center and exits through the collection tube¹³. The membrane area of one small laboratory spiral wound module is typically 0.2-1.0 m², whereas that of industrial-scale module is up to 20-40 m².



Figure 3. Spiral Wound module for CO₂ separation application: (A) element configuration and (B) module construction

Spiral-would membrane configuration has a standard manufacturing which makes their installation easier with less cost in membrane production. The installation of these configurations can be performed in series or parallel in plants with higher capacity¹¹.

¹³ R. W. Baker, Membrane Technology and Applications. 2012.



2.2.3 Hollow fiber

Hollow fiber structure is preferred for large scale applications due to large membrane surface area per unit volume, good flexibility, easy handling, and easier module fabrication¹⁴. Additionally, hollow fiber membranes provide mechanical support (module) and are easier to handle both in fabrication and separation process operation⁸. From all types of membranes, asymmetric hollow-fiber (fabricated with different thickness of substrate and separation layer), are the ones preferred as they enhance productivity and reduce the cost of membranes in gas separation technology¹⁵.

One type of the hollow fiber membrane module for CO_2 separation applications is illustrated in Figure 4. The module consists of bundles of fibers enclosed in a pressure vessel, with the permeate gas passing either out of the fibers (bore-side feed) or into them (shell-side feed). Optimization of hollow fiber modules for specific applications involves selection of flow patterns and flow direction of shell versus fiber. Chung et al. recently reported various module configurations and flow configurations for the design and fabrication of hollow fiber membrane.



Figure 4. Hollow fiber membrane module structure¹⁶

The (outside) diameter of hollow fibers is typically lower than 1000 μ m, depending on the application. Fibers can be made from one or two materials. Two layers are used for the outside or inside surface. The selective layer can be integrated with the fiber or a separate one coated on a porous support (fiber). Outside diameter of 50 to 200 μ m is normally named fine hollow fibers. High-pressure gas separations usually need these fine fibers because they can resist very high outside hydrostatic pressures up to 1000 psig. For low-pressure gas separations, a fluid is generally put inside the fiber, while the permeate is placed in the outer shell. The fiber diameter is usually greater than 200-500 μ m. The fibers are called capillary fibers if the diameter is above 500 μ m⁸.

Hollow fiber membrane bundle is fixed in a module so that the gas concentration gradient in the gas flow direction is almost constant and to limit short-cuts. The gas is generally compressed to a certain pressure before entering the module. The feed gas must be free of particles and liquids because these undesired components must not enter compression devices. Hence, gas mixture separation process by hollow fiber modules does not required further pre-treatment⁸.

¹⁴ C. Hun and e. al., "Orientation of an Amphiphilic Copolymer to a Lamellar Structure on a Hydrophobic Surface and Implications for CO2 Capture Membranes," Membranes, vol. 131, p. 1155–1159, 2014.

¹⁵ X. Chen, G. Liu and W. Jin, "Natural Gas Purification by Asymmetric Membranes: An Overview," Green Energy & Environment, 2020.

¹⁶ Stephen A. Rackley, 8 - Membrane separation systems, Carbon Capture and Storage (Second Edition), Butterworth-Heinemann, 2017, Pages 187-225, ISBN 9780128120415.





Figure 5. Schematic of a hollow fiber membrane

2.3 Membrane materials

The materials selected for membrane fabrication are directly related to the specific requirements of each application, such as permeability, selectivity towards the desired components, surface area, cost. To date, only polymeric membranes have been commercially available and applied to biogas and natural gas. However, polymeric membranes have limited performance and they are susceptible to plasticization. Over the years, other type of materials has been investigated for the fabrication of membranes with improved characteristics. Membranes on this report are referring to CO_2 separation.

2.3.1 Polymeric membranes

Currently polymeric materials are dominant in the market for gas separation applications. However, polymeric membranes have limited performance mainly due to the permeability/selectivity trade-off as well as their susceptibility to plasticization at high pressure or long-time exposure period⁸. The transport mechanism of gas molecules through the polymeric membranes is by a solution-diffusion mechanism, while others include molecular sieve effect, and Knudsen diffusion mechanisms⁴.

The selection of polymer materials to make membrane for gas separation applications depends on the polymer chemical resistance, as well as sorption capacity and mechanical resistance. Other important requirements include:

- Intrinsic polymer perm-selectivity
- Swelling resistance to membrane plasticization
- Film processability into asymmetric morphology.

To overcome polymers' Roberson upper bound limit, mixed-matrix membranes (MMM) have been proposed, to incorporate inorganic materials such as zeolites, metal organic frameworks (MOFs) and various nanoparticles into the polymer matrix¹⁷.

¹⁷ F. Karamouz and H. Y. R. Maghsoudi, "Synthesis and characterization of high permeable PEBA membranes for CO2/CH4 separation," Journal of Natural Gas Science and Engineering, vol. 35, pp. 980-985, 2016.

2.3.1.1 Poly-ethylene oxide (PEO) based membranes

Especially for CO_2 capture, poly-ethylene oxide is proven to be a good candidate material for membrane fabrication. Poly-ethylene oxide (PEO)-based polymers show a considerable CO_2 solubility, and the CO_2 selectivity mainly stems from the solubility selectivity. One drawback, however, is that the polar ether groups tend to form strong hydrogen bonding, which induces compact chain packing. A high degree of crystallinity has also been reported in pure PEO or PEO-based materials¹⁸.

To overcome these limitations, various approaches have been devised, including block copolymerization with other hard segments, blending with low molecular weight poly-ethylene glycol (PEG) and PEG-derivatives, and crosslinking to form highly branched PEO polymer network. These concerted efforts not only produced considerably permeable PEO-based membrane materials, but also led to a deep understanding of the nanostructures of the PEO-based polymers¹⁸. Table 4 summarizes the CO₂ permeabilities and CO₂/gas selectivities of the PEO-based polymers synthesized based on different strategies. The CO₂ permeances of a few membranes in thin-film composite configuration are also listed.

Strategy	Material	p(CO ₂)/atm	T/ºC	P(CO ₂)/Barrer	a(CO ₂ /N ₂)	a(CO ₂ /CH ₄)	a(CO ₂ /H ₂)
Copolymer	PEO-b-PA6	10	35	120	51.4		9.8
	PEO-b-PBT	0.3	30	150	51.5	16.8	10.3
	PEO-g-POEM	1	35	147	47		
	PEO-ran-PPO-T6T6T	4	35	470	43	13	10
	GPA1000-g-PEG-azide	2	45	1840	36		8.3
	PEO-b-PBT on PDMS	5	30	1815*	50		
	PEO-b-PS	1	70	20400*	27.7		
Blending	PEBAX®1074/PEG1500	5	60	528	34.6	7.4	10.6
	PEBAX® MH1657/PEGDME500	0.3	30	650			14.9
	PEBAX® MH1657/PEG-AE	0.3	30	335			12.9
	PEBAX® MH1657/PEG-DVE	0.3	30	570			12.9
	PEBAX® MH1657/PEG-AME	0.3	30	620			14.5
	PEO-PPO-T6T6T/PDMS-PEG	4	35	896	36	10.9	10.6
	PEBAX® 1657/PEGDME500	0.17	57	940*	30		
	PEBAX® 2533/PEG-b-PPFPA	3.5	35	940*	17		
Crosslinking	PEGDA/PEGMEA	11	10	300		23	
	PEGDA/PEGMEA	4	35	570	41		
	PEGDA/TRIS-A	15	35	716	19.9		7.7
	PEA/TMC	0.2	25	360*	67.2		
	DGBAmE/TMC	0.71	22	1310*	33		

Table 4. Transport properties of selected PEO-based polymers¹⁸

p(CO₂)= CO₂ partial pressure; P(CO₂)= CO₂ permeability; a=ideal CO₂/gas selectivity;

*Permeance measured in thin0film-composite membrane, GPU

The first few ground-breaking copolymers were under the commercial names Pebax® and Polyactive[™], in which various polyamides (PA) and poly-butylene terephthalate (PBT) served as the hard segments, respectively¹⁹. Pebax® is a commercial polyether-polyamide copolymer membrane. Pebax® MH1657

¹⁸ Han, Y., & Winston Ho, W. S. (2018). Recent advances in polymeric membranes for CO2 capture. Chinese Journal of Chemical Engineering. vol. 26. p. 2238–2254.

¹⁹ Y. Chen and e. al., "New Pebax®/zeolite Y composite membranes for CO2 capture from flue gas," Journal of Membrane Science, vol. 495, pp. 415-423, 2015.

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Co Mem	-BASED USTRIES C-Privat Perbandia	Industrial membrane requirements	DLR-WPL-3 Date: Page Nº:	30112020-v01.pdf 03/11/2020 16 of 74

blended with poly-ethylene glycol of low molecular weight for gas separation in several experiments has shown results in permeability of 79 to 378 Barrer, and ideal selectivity of 16.8 to 14.3 for CO₂ removal. Until now, no significant improvements in gas separation properties have been shown for other copolymerization modified membranes¹⁸. Ultrathin composite membranes were also synthesized by this approach. Chen et al. reported a Pebax®-based membrane with (polyethylene glycol)dimethyl ether (PEGDME-500) coated on deposited zeolite-Y nanoparticles¹⁹. The membrane demonstrated a CO₂ permeance of 940 GPU with a surprisingly high CO₂/N₂ selectivity of 30 at an elevated temperature of 57 °C. PEBA membranes can be designed for both layer and hollow fiber configurations. Table 5 describes two alternatives for CO₂ separation commercially existing in the market.

Table 5	Dolucthow	blook amida	(DEDA)	based	mambuanaa	for CO	acompanyation 18
I able 5.	Polvetner	роск анние	FEDAL	Daseu	memoranes	10f UU2	separation
			· · ·				

Membrane	Gas mixture	Membrane Feature	Process performance	Main remarks
Commercially	Pure gases	Membrane	Permeability (Barrer):	The permeability of CO ₂ in
available	(H ₂ , N ₂ , CH ₄ ,	Thickness $= 60-100$	$CO_2 = 73-151$	Pebax®/PEG membrane (50 wt.% of
Pebax®	CO ₂)	mm	Permeance (GPU): CO ₂ <2.5.	PEG) is twofold regarding to the
MH1657 and its			Selectivity:	pristine Pebax® and an enhancement
blends with low			$CO_2/N_2 = 43-47$	of CO ₂ /H ₂ selectivity of ~11 is
molecular			$CO_2/CH_4 = 15.1-15.9$	produced due to the presence of EO
weight PEG			$CO_2/H_2 = 9.1-10.8$	units that increases CO ₂ permeability.
Hollow fiber	Pure gases:	Membrane	Dense PEBA membranes:	CO ₂ permeability tends to increase
PEBA/PSf	CO ₂ ; N ₂	thickness = 55 mm	Permeability (Barrer):	with an increase in gas pressure due to
composite		Layer (PEBA)	$CO_2 = 200-550$	plasticization of the membrane caused
membranes and		Thickness < 5 mm	$N_2 = 8-36$	by the relatively high solubility of
dense PEBA			Selectivity:	CO2 in the membrane. But the
membranes			$CO_2/N_2 = 16-40$	plasticization and swelling of the
			Composite membranes:	membrane are less significant at
			Permeance (GPU):	higher temperatures.
			$CO_2 = 61$	The selectivity of the composite
			Selectivity: $CO_2/N_2 = 30$	membrane is very close to the intrinsic
				selectivity of PEBA dense membrane.

2.3.2. Inorganic membranes

Inorganic membranes are based on different materials like metal (alumina, cobalt, copper, iron, nickel, niobium, palladium, platinum, tantalum and vanadium), zeolites, carbon, and ceramic, among others. Generally, these membranes show higher gas separation performances combined with substantial chemical and thermal stability. However, these materials have poor mechanical properties and are difficult to process. Moreover, considering that those materials are brittle and their production is expensive, their conversion into high surface area modules is rather difficult²⁰.

Inorganic membranes have shown great interest within the scientific community. In fact, the last decade some inorganic membranes have been exploited with excellent selectivity for specific gas separation, with some applications close to commercialization. Table 6 presents the main materials for membrane gas separation⁸.

Table 6. Organic polymers and inorganic membrane materials⁸

Organic polymers	Inorganic materials
Polysulfone, polyethersulfone	Carbon molecular sieves
Cellulose acetate	Nanoporous carbon

²⁰ R. Vijay and e. al., "Evaluation of biogas upgrading technologies and future perspectives: a review," Environmental Science and Pollution Research, vol. 26, p. 11631–1166, 2013.



Polyimide, polyetherimide	Zeolites
Polycarbonate (brominated)	Ultramicroporous amorphous silica
Polyphenylene oxide	Palladium alloys
Polymethylpentene	Mixed conducting perovskites
Polydimethylsiloxane	Metal organic frameworks
Polyvinyltrimethylsilane	

2.3.3. Carbon Molecular Sieve

Carbon molecular sieve (CMS) membranes have been considered as a kind of high-performance gas separation membrane. A CMS membrane is a porous solid membrane with extreme rigidity and microporosity. The gas molecules are separated by the size sieving effect, in contrast with polymeric membranes; the gas molecules of certain sizes that are smaller than the critical distance can pass, whereas those gas molecules larger than the critical distance, d_c , will be rejected. Other differences of CMS with polymeric membranes can be seen in Table 7²¹.

Table 7. The difference between CMSMs and polymeric membranes²¹

	Polymeric Membrane	CMS Membrane
Separation performance	Good to high	High
Separation mechanism	Solution-diffusion	Molecular sieve
Advantages	Low production cost, Excellent chemical stability,	
	Mass production	Surpass the trade-off curves
		Excellent thermal stability,
		Can be used under aggressive conditions
Disadvantages	Poor thermal and chemical stabilities,	Brittle,
	Relatively low performance	High cost

Especially for the natural gas application, CMS hollow fiber membranes have been a promising candidate based on the molecular sieving effect. This kind of membranes present with good separation performance and are tunable to parameters such as pyrolysis temperature, inert gas atmosphere, final temperature, and thermal soak time etc. For industrial application, it is necessary for CMS asymmetric membranes to possess high mechanical strength and maintain high performance under harsh operating conditions. Attention should be paid to physical and chemical aging. Overall, CMS presented with good balance between tunability, scalability and separation performance. However, in order to be competitive in the natural gas purification, the production cost is still ought to be addressed¹⁵.

CMS's selectivity increases when the micropores of CMS are narrower, which could be achieved by high temperature drying process to carbon hollow fiber membranes (CHFM). This results to a stronger resistance to the larger gas molecules, such as CH₄, but also causes a decrease of gas diffusion coefficient. It is reported than a reduction of the micropores from 6 to 4.9 Å to an enhancement of CO_2/CH_4 ideal selectivity up to 917 when tested at 2 bar for the CHFM-140°C²².

²¹ Xiao-Hua Ma, Shi-Yong Yang, Chapter 6 - Polyimide Gas Separation Membranes, Editor(s): Shi-Yong Yang, Advanced Polyimide Materials, Elsevier, 2018, Pages 257-322, ISBN 9780128126400.

²² L. Lei, A. Lindbråthen, X. Zhang, E. P. Favvas, M. Sandry, M. Hillestad and X. He, "Preparation of carbon molecular sieve membranes with remarkable CO2/CH4 selectivity for high-pressure natural gas sweetening," Journal of Membrane Science, vol. 614, 2020.

Bi			D2.2	Proj. Ref.: Doc. Ref.:	BIOCOMEM-887075 BIOCOMEM-WP2-D2.2-
Co	6	****	Industrial membrane requirements	DLR-WPL-3	30112020-v01.pdf
Mem	BIO-BASED	****	_	Date:	03/11/2020
TVICITI	* * Public-Private Partnership			Page N ^o :	18 of 74

Recently, carbon membranes made from polyimide precursors were tested at high pressure of up to 120 bar for CO_2/CH_4 separation²³. They reported a CO_2 permeance of 100 GPU (i.e., 0.28 m³(STP)/(m²·h·bar)) and a CO_2/CH_4 separation factor of 60 based on a 50% $CO_2/50\%$ CH₄ gas mixture permeation testing, which may have the potential for natural gas sweetening²⁴.

Regenerated cellulose-based CMS membranes where tested in a pilot plant in Norway to upgrade biogas into vehicle fuel. After H_2S and H_2O removal in pretreatment, the CMS hollow fibers displayed 97 mol% CH₄ as well as 98% CH₄ recovery in a single stage process and performed stably in 8 days, which indicates the feasibility of CMS hollow fibers for industrial application²⁵.

Membrane	Feed gas CO ₂ /CH ₄	Feed pressure (bar)	CO ₂ permeance (GPU)	CO ₂ /CH ₄ selectivity
6FDA/BPDA-DAM CMS HF	10/90 (vol%)	3.40	30	73
Matrimid 5218 CMS HF	10/90 (vol%)	3.40	12	69
6FDA/BPDA (1:1)-DAM CMS HF	50/50 (vol%) and 500ppm C7 HC	124.13	50	~60
ULT CMS-6F0.5 HF	50/50 (mol%)	6.90	2546	24.10
6FDA:BPDA-DAM CMS HF	Pure gas	0.34	273	32

Table 8. Performance of asymmetric membranes for natural gas purification¹⁵

2.3.4. Mixed Matrix Membranes

Mixed matrix membranes (MMM) consist of an organic polymer combined with inorganic (or sometimes organic) particles. The dispersed phase may be zeolites, carbon molecular sieves (CMS), carbon nanotubes (CNT) or other nano-size particles. Metal organic frameworks (MOFs) are a newer class of crystalline and porous materials and are now used to overcome the limitations of inorganic membranes. Today, several investigations of MMM technology combining the advantages of inorganic fillers with the acceptable mechanical properties and cost-effective processability of polymers were performed for CO₂/CH₄ gas separation⁸. Thus, MMM have attracted great interest as they present potential for high selectivity, high permeability or both, compared to actual polymer and inorganic membranes.

It should be noted that the performance of MMM is not the sum of the intrinsic properties of each individual component²⁶ and in fact, the performance can be seriously affected by the complex interaction between all parameters. Transport properties of MMM are highly function of membrane morphology at the nanoscale, which is critical for the overall membrane properties⁸.

Figure 6 displays the different nano-scale structures of the interface between the polymer and the particles. *Case I* is an ideal morphology and difficult to get with perfect adhesion at the filler-polymer interface. *Case II* is a situation where the pores have been partially blocked at the surface of the particles by polymer chains. *Case III* shows that polymer molecules in direct contact with the zeolite surface are rigidified (limited mobility) compared to the bulk polymer. *Case IV* represents the detachment of polymer molecules from the

²³ C. Zhang, G. B. Wenz, J. Williams, J. M. Mayne, G. Liu and W. J. Koros, "Purification of Aggressive Supercritical Natural Gas Using Carbon Molecular Sieve Hollow Fiber Membranes," Industrial & Engineering Chemistry Research, 2017.

²⁴ X. He, I. Kumakiri and M. Hillestad, "Conceptual process design and simulation of membrane systems for integrated natural gas dehydration and sweetening," Separation and Purification Technology, vol. 247, 2020

²⁵ S. Haider, L. Arne, A. J. Lie, P. Vattekar Carstensen, J. Thorbjorn and H. Britt, "Vehicle fuel from biogas with carbon membranes; a comparison between simulation predictions and actual field demonstration," Green Energy & Environment, vol. 3, no. 3, pp. 266-276, 2018

²⁶ DIBLÍKOVÁ, P., VESELÝ, M., SYSEL, P., & ČAPEK, P. (2017). Reconstructing the microstructure of polyimide-silicalite mixed-matrix membranes and their particle connectivity using FIB-SEM tomography. Journal of Microscopy, 269(3), 230–246.



particles surface producing voids at the interface. Other possible reasons for voids formation include repulsive forces at the polymer/filler interfaces, as well as different coefficients of thermal expansion⁸.



the nanoscale in MMMs. 154x159mm (300 x 300 DPI

In order to inhibit the mobility of polymer chains in the contact region with the particles, besides rigidification effect (Case III), another possible way is by increasing the permeation activation energy can also reveal lower chain mobility (rigidification). As a result, increase of selectivity leads to a decrease in permeability quickly in MMM. The glass transition temperature (Tg) can be used to determine whether rigidification in the MMM occurs or not. It is well-known that Tg can qualitatively be used to estimate polymer chains flexibility. Therefore, MMM with rigidified polymer chains, have higher Tg compared to the base polymer^{8,27}.

Reduction of surface area of porous fillers can be associated to pore obstruction by polymer molecules (Case II) in MMM. Depending on pore size, polymer chains can enter the pores at different levels or even make complete blockage. Pore blockage always causes a decrease in gas permeability, the selectivity relying on the type of particles used. Smaller particles give more interfacial area between the polymer and particles, potentially making better MMM. Moreover, thinner MMM can be made by using smaller particles⁸.

Particle agglomeration due to sedimentation and migration to the surface is an important problem for the manufacture of MMM. Differences in density and other physical properties between the zeolite and the polymer can lead to spatial distribution problems. Zeolite precipitation may even occur. Agglomeration of zeolites may also cause pitting and forming non-selective defects in MMM. To solve this problem, increased solution viscosity, use of ultra-thin crystallites, and control of drying conditions are applied during membrane manufacture⁸.

2.3.4.1. Mixed matrix membranes composed of polymers and zeolites

A zeolite is a crystalline microporous aluminosilicate having large cations and water molecules with high freedom of motion. This can allow good ion-exchange and reversible dehydration properties. Over 150 different zeolite crystal structures are known today. Most of them are synthetic materials, but some of these structures also occur as natural geological materials. Many types and zeolite families have been made and used for gas separation²⁸. For adsorption, interaction with highly polar surface within the pores is the main driving force in zeolites. CO₂ adsorbs more strongly than H₂, CH₄, and N₂ on zeolites because of electrostatic quadrupole moment and molecular weight of CO₂ are higher than others light gases.

²⁷ Awe, O.W., Zhao, Y., Nzihou, A. et al. A Review of Biogas Utilisation, Purification and Upgrading Technologies. Waste Biomass Valor 8, 267–283 (2017).

²⁸ D. Bastani and e. al., "Polymeric mixed matrix membranes containing zeolites as a filler for gas separation application": A review," Journal of Industrial and Engineering Chemistry, p. 375–393, 2013.



Linde Type A (LTA), Faujasite (FAU), Chabazite (CHA) and Mordenite (MOR) zeolites have high CO₂ heat of adsorption²⁹. This unique property results in high CO₂ adsorption capacity even at low concentration. Adsorption on zeolites is dependent on the following physical molecular properties:

_	Size and shape: Gas molecules smaller than the pore size can adsorb on zeolites, whereas larger gas molecules cannot.
	 Small pore size (0.30-0.45 nm). These zeolites have 8 membered-rings pore apertures with free diameters like zeolite NaA. Medium pore size (0.45-0.60 nm). These zeolites have 10 membered ring apertures, within free diameter like zeolite ZSM-5. Large pore size (0.6-0.8 nm). These zeolites have 12 membered-ring apertures or more within free diameter like zeolite faujasite (X, Y).
—(Molecular polarity:
	• Gas molecules with higher polarity can be better adsorbed than non-polar gas for the majority of zeolites under identical conditions.
-(Counter-ion:
	• The type of cation controls the electric field inside the pores, basicity, and the available pore volume, which offers a convenient means for tuning adsorption properties.

Figure 7. Physical molecular properties of zeolites

In zeolite filled MMM, the zeolites exhibit higher penetrant sorption capacities and improved penetrant size-based selectivities for gas molecules than polymers. This is due to the large micropore volume and to the molecular sieving effect of the pore windows. In order to enlarge the application range of MMM, a more efficient membrane geometry was developed which is the asymmetric hollow fiber membranes. The hollow fiber structure is preferred due to large membrane surface area per unit volume, good flexibility, easy handling, and easier module fabrication²⁸.

2.3.5. Fixed-site carrier membranes

Facilitated transport membranes (FTM) exhibit "solution-diffusion" characteristics and also contain an active transport mechanism that increases the permeability and selectivity of the membrane material. The target species reversibly reacts with either a fixed or mobile carrier present in the membrane that then diffuses across the membrane driven by a concentration gradient in the complex rather than a gradient in the permeate. Unlike non-facilitated transport membranes, the main characteristic of these membranes is represented by the decrease of both CO_2 permeance and selectivity with increasing CO_2 feed partial pressure. A schematic representation of the mechanisms for a fixed carrier amine based facilitated transport membrane is provided in Figure 10. As shown, the CO_2 is absorbed and reacts to form bicarbonate, the form in which it permeates the membrane. Upon reaching the other side it back reacts to form CO_2 and is then released on the permeate side.

PVAm has been the most studied polymers. Wang et al. developed a series of facilitated transport membranes with an ultrathin selective layer via solution coating or interfacial polymerization. The effects

²⁹ Karkhanechi, Hamed & Kazemian, Hossein & Nazockdast, Hossein & Mozdianfard, M.R. & Bidoki, Seyed. (2012). Fabrication of Homogenous Polymer-Zeolite Nanocomposites as Mixed-Matrix Membranes for Gas Separation. Chemical Engineering & Technology. 35.

Bi	Ø	****	D2.2 Industrial membrane requirements	Proj. Ref.: Doc. Ref.: DLR-WPL-3	BIOCOMEM-887075 BIOCOMEM-WP2-D2.2- 30112020-v01.pdf
Mem	* BIO-BASED NDUSTRIES	****	-	Date: Page Nº:	03/11/2020 21 of 74

of representative contaminant SO_2 on the performance of membranes containing amino groups have been also intensively investigated. Hägg et al. (2009) also investigated the possibility of post-combustion CO_2 capture using PVAm-based membranes in the laboratory-scale and pilot-scale with both flat sheet membranes and hollow fiber membranes.



Figure 8. Schematic of the mechanism for a fixed carrier amine based facilitated transport membrane

Fixed-site-carrier (FSC) membranes is a type of facilitated transport memebranes developed by coating a thin selective polyvinylamine (PVAm) layer on top of polysulfone (PSf) ultrafiltration membrane for CO_2/N_2 separation in the Memfo group at NTNU. The FSC membranes can be used in humidified condition, which can be considered as an advantage for the flue gas application as dehydration can be avoided in post combustion CO_2 capture. These membranes have been further tested in pilot scale for CO_2 capture from flue gas in power plant for the NanoGLOWA EU project³⁰.

In 2014, a hybrid FCS was tested, coating carbon nanotubes in the FSC. Small pilot-scale modules with membrane area of 110-330cm² were tested with high pressure permeation rig. The prepared hybrid FSC membranes show high CO₂ permeance of $0.084\sim0.218$ m³ (STP) / (m².h.bar) with CO₂/ CH₄ selectivity of 17.9-34.7 at different feed pressures up to 40 bar for a 10% CO₂ feed gas. Simulation and technoeconomic analysis indicated that the developed FSC membranes could be a promising candidate for CO₂ removal from low CO₂ concentration (10%) natural gases with a low natural gas sweetening cost of 5.73×10^{-3} \$/Nm³ sweet NG produced³¹.

³⁰ X. He, Lindabrathen and T.-J. H. M.-B. Kim, "Pilot testing on fixed-site-carrier membranes for CO2 capture from flue gas," International Journal of Greenhouse Gas Control, vol. 64, pp. 323-332, 2017.

³¹ H. He, M.-B. H. Hagg and T. J. Kim, "Hybrid FSC Membrane for CO2 Removal from Natural Gas: Experimental, Process Simulation and Economic Feasibility Analysis," AlChe Journal, vol. 60, no. 12, pp. 4171-4184, 2014.



3 NATURAL GAS SWEETENING

Natural gas comes in many different forms, that all have distinct and shifting qualities. As a result, different types of natural gas have been used in the EU, rather than one type of gas with one specific quality. This can cause problems in an integrated energy market, as suppliers in one country risk having their gas rejected by transmission system operators in another because the gas does not have the right quality. This difference in gas qualities can moreover affect whether household and industrial products are used in a safe manner³². The European Commission has issued a mandate to the European Committee for Standardisation (CEN) to draw up harmonised standards for gas quality in the EU.

This chapter aims to review the membrane systems applied for separation of CO_2 in natural gas streams, process commonly known as natural gas sweetening, with a special focus on polymer membranes (copolymer PEBAs), as well as its industrial requirement for hollow fiber configurations. Although different membranes could probably be used in a specific natural gas separation process, choosing a suitable membrane material will mainly depend on the membrane permeance and selectivity, process conditions (e.g., operating pressure, temperature) and impurities in the gas stream (such as SO_2 , hydrocarbons, NOx, H_2S , etc.).

3.1 Natural gas applications

Raw natural gas varies substantially in composition from source to source. Methane is always the major component, typically 75%-90% of the total, but natural gas also contains significant amounts of ethane, some propane and butane, and 1%-3% of other higher hydrocarbons³³. In addition, the gas contains undesirable impurities, such as water, carbon dioxide, nitrogen, and hydrogen sulphide. Although the composition of raw gas varies widely, the composition of gas delivered to commercial pipeline grids is tightly controlled. Few examples of the composition of natural gas can be seen in Table 9, while typical European natural pipe specifications are shown in Table 9.

Component	Groningen (Netherlands)	Laeq (France)	Uthmaniyah (Saudi Arabia)	Ardjuna (Indonesia)	Uch (Pakistan)
CH4	81.3	69	55.5	65.7	27.3
C ₂ H ₆	2.9	3	18	8.5	0.7
C3H8	0.4	0.9	9.8	14.5	0.3
C4H10	0.1	0.5	4.5	5.1	0.3
C5+	0.1	0.5	1.6	0.8	
N2	14.3	1.5	0.2	1.3	25.2
H ₂ S		15.3	1.5		
CO ₂	0.9	9.3	8.9	4.1	46.2

Table 9.	Composition (of natural gas	s reservoirs in	some narts of t	the world in	volume n	recent basis ³⁴
rabic /.	composition	or matur ar Sas	, i coci von o m	some parts or o	ine worra m	voiume p	i ccent basis

 $^{^{32}\ \} Mandates\ \ for\ \ harmonization.\ \ https://ec.europa.eu/energy/topics/markets-and-consumers/wholesale-market/gas-quality-harmonisation$

³³ R. Baker and L. Kaaeid, "Natural Gas Processing with Membranes: An Overview," Ind. Eng. Chem., vol. 47, pp. 2109-2121, 2008.

³⁴ Al-Megren, H. A. (2012). Advances in natural gas technology. Rijeka, Croatia: InTech.



Component		Unit	Russian gas	North Sea gas	Danish gas	Dutch gas	German gas
Methane	CH4	mol%	96.96	88.71	90.07	83.64	86.46
Nitrogen	N ₂	mol%	0.86	0.82	0.28	10.21	10.24
Carbon dioxide	CO ₂	mol%	0.18	1.94	0.60	1.68	2.08
Ethane	C ₂ H ₆	mol%	1.37	6.93	5.68	3.56	1.06
Propane	C ₃ H ₈	mol%	0.45	1.25	2.19	0.61	0.11
Butanes	C4H10	mol%	0.15	0.28	0.90	0.19	0.03
Pentanes	C5H12	mol%	0.02	0.05	0.22	0.04	0.01
Hexanes and higher	$C_{6}+$	mol%	0.01	0.02	0.06	0.07	0.01
Oxygen	O2	mol%	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Total sulphur	S	mg/m ³	< 3	< 5	< 3	< 3	< 3

Table 10. Typical compositions of natural gas used in Europe (0 °C, 1.01325 bar)

3.2 Market size

Every year, the world uses close to 3937³⁵ bcm (billion cubic meters) of natural gas, driving a worldwide market for new natural gas separation equipment of ~\$5 billion per year. All of this gas requires treatment before it enters the pipeline, making natural gas processing, by far, the largest market for industrial gas separation as well as an opportunity for membrane technology applications. By 2008 membrane processes have had less than 5% of natural market, almost all of which is applied toward the removal of carbon dioxide³³. Nevertheless, membranes are becoming a competitive technology compared to the conventional separation unit operations, e.g. chemical and physical absorption with amines. In fact, membrane technology competes most directly against absorption for carbon dioxide removal.

3.3 System providers

Membrane companies entered the natural gas processing industry in the 1980s, offering systems for carbon dioxide removal in competition with amine absorption. The first membrane systems to separate carbon dioxide from natural gas were introduced by Grace Membrane Systems (a division of W.R. Grace), Separex (now part of UOP), and Cynara (now part of Natco)^{33,36}. These companies used anisotropic cellulose acetate membrane that was produced using the Loeb-Sourirajan technique, a precipitation process where the same polymer is used for the selective layer and the microporous support layer (e.g. cellulose acetate membranes are still widely used).

Among the various membrane system suppliers, there are several of them providing for the natural gas application. The following list highlights those suppliers, the materials and configurations used, as well as brief information with respect to the description of their systems.

System Provider	Module type/Material	Module configuration	Description
Air Liquide	MEDAL and PoroGen PEEK- sep	Parallel multi-module system	MEDAL large diameter 12" membranes fit more surface area into a given volume, which requires less steel, thereby lowering system cost.
	Hollow fibers.	Every 12-inch module contains 0.5-1.0 million fibers	PoroGen PEEK-Sep membranes can operate with thermo-mechanical properties and chemical resistance in condensing mode with minimal pre-treatment, such as:

Table 11. Membrane system providers for natural gas

³⁵ Referenced data from 2018 (iea) https://www.iea.org/fuels-and-technologies/gas

³⁶ R. Baker, "Future Directions of Membrane Gas Separation Technology.," Ind. Eng. Chem., vol. 41, pp. 1393-1411, 2002



	Asymmetric small diameter porous tubes made of polyimide and PEEK polymers.		Feed >> Coalescing filter >> membrane process >> Product. The hollow fiber dimensions and pore size are tailored towards the target gas purification.
Atlas Copco	p <i>j</i>		
Evonik Industries AG	SEPURAN [®] NG Hollow fiber membrane based on a high- performance polymer	8" Plug-in membrane modules consisting of a cartridge cast and a vessel. Typically, 3 to 5 cartridges are connected in series in the same housing	The membrane is designed for the challenging process conditions of natural gas processing with complex gas compositions and typical pressure and temperature conditions up to 70°C. It can be used particularly effectively in natural gas sources with a high concentration of carbon dioxide because, under these conditions, the separating properties of the membrane remain intact
Honeywell Uop LLC	Separex [™] UOP Separex [™] Spiral-Wound or Hollow Fiber can be found in different materials: • Cellulose Acetate (CA). • Polyimide (PI). • Polyamide. Polysulfone. • Silicone Composite Membranes	One-stage and two-stage, for both systems a recycle compressor is needed. Hybrid (amine-membrane) able to treat feed flow between 5-900 MMSCFD.	 Modular, skid-mounted units to treat economically: Feed flow of >5 MMscfd Feed pressure of ~138 barA Permeate pressure of ~3.5 barA Feed temperature of 16°C to 65°C The system requires Pre-treatment train as: Feed >> Filter coalescer >> Heater >> Non-regenerative Absorbent >> Particle filter >> membrane to remove heavy HC's compressor oils, well additives and pipeline corrosion inhibitors.
Parker- Hannifin Corporation			
Schlumberger	CYNARA Hollow fibers made from cellulose triacetate polymer.		CYNARA acid gas removal membrane systems efficiently and selectively permeate acid gases to separate them from produced gas streams that contain 5- to 95-mol% acid gas. Operation references of 1200 MMscfd and higher, CO ₂ inlets from 5- 85% and CO ₂ outlets from 1.5-50%. The need to superheat gas streams containing >40% CO ₂ and related costs are also minimized because the membranes can efficiently handle condensing hydrocarbons. CYNARA systems use tubular membrane elements that consist of a central steel tube surrounded by a sheet of asymmetric, hollow fibers, which are combined to make a single element, which is housed in a case.
UBE Industries Ltd	Separation Membrane Hollow fiber membrane made of aromatic polyimide.	 One-stage: Outlet gas composition: 1.8%v CO2, 87%v CH4, 9.3%v C2+, 1.9%v N2. Flow rate inlet gas 20 MMscfd at 950 psig Two-stage. Retentate stream of the 2nd stage recycled back to the inlet of the 1st stage. Outlet gas composition: 	 The gas mixture is introduced to the outer side of hollow membrane at a pressure of around 2200 psig, and the pressure of the other side of the membrane is maintained at a lower value. Easy permeable gas components like CO₂, H₂O and H₂S permeate through the membrane, while gas components like hydrocarbons are remained in the outer side of the membrane. Because of high thermal resistance of polyimide, the membrane can be operated up to 100 °C. By applying higher operation temperature compaction can be minimized, also once declined permeability can be recovered.



		 1.9%v CO2, 97.6%v CH4, 0.4%v C2+, 0.1%v N2. Flow rate inlet gas 100 MMscfd at 850 psig The modules are available in: ID: 4" – 8" inches Length: 80 – 160 inches 	UBE's polyimide Membrane System applies only 1/2 to 1/4 membrane modules compared to the conventional relevant systems. Therefore, these systems are the most compact among available membrane systems. Also, because of excellent durability against contaminants, only a simple pre-treatment of the raw natural gas is required.Both membrane systems require heating up the feed stream and can be integrated with absorption process for CO2 enrichments.
ProSep	Natural gas Membranes Flat sheet formed by packaging several of these flat sheets into a spiral wound module.	One-stage and two-stage systems. For the two-stage, compression of the permeate stream before entering the 2 nd stage is required.	 ProSep's membrane systems successfully treat feed gas that contain a range between 3% - 88% %mol acid gases. Membranes separation is driven by the component partial pressure difference across the membrane layers. The system includes a pre-treatment skid with: Coalescing filters Activated carbon adsorbent Polishing filters Thermal swing adsorption (TSA) units Mechanical refrigeration units
Fujifilm	<u>ApuraTH</u> Spiral wound, multilayer	Available in 8-in and 8.25- in-diameter sizes.	Apura membranes removes CO ₂ , H ₂ S, H ₂ O and N ₂ . Range of operation between 5-150 bar, 0-50°C
	composite membranes in combination with	Performance of two-stage systems can achieve up to 99% hydrocarbon recovery.	equipment, like amine plants, as well as at remote sites.
	polymers		content in the permeate stream and maximum hydrocarbon recovery.

3.4 Technology overview for natural gas separation

CO₂ is characterised for reducing the heating value of natural gas, is corrosive and easily forms hydrates. For these reasons, CO₂ removal from natural gas is mandatory to potentially avoid clogging of equipment, damage pumps, minimize corrosion in the pipelines and to meet gas grid specifications^{3,33}. Choosing a suitable technology for CO₂ removal from natural gas is mainly dependent on process conditions and crude natural gas composition. Traditional chemical (amine) absorption-stripper technology has the bulk of the carbon dioxide natural gas treatment market and is still considered as a state-of-the-art technology³. However, this is costly process with high footprint. Membranes come as a cost-effective and environmentally friendly solution for the gas separation industry. Other technologies have also been identified for acid gas removal, including using a liquid desiccant to absorb the acidic gases, using a solid desiccant to adsorb the acidic gases, cryogenic distillation and direct conversion by chemical reactions³⁷. Table 12 presents a brief classification of the technologies.

Table 12. Classification of natural gas sweetening technologies³⁸

CO2 removal mechanism	Process type	Technology	Commercial name
Chemical absorption	Regenerative, continuous	Amines	MEA, DEA, MDEA, DIPA, DGA,
		Potassium carbonate	Benfield, Catacarb, Giammarco-
			Vetrocoke, etc.

³⁷ G. George and e. al., "Polymer membranes for acid gas removal from natural gas," *Separation and Purification Technology*, vol. 158, pp. 333-356, 2016.

³⁸ I. T. Marco Bergel, "SWEETENING TECHNOLOGIES – A LOOK AT THE WHOLE PICTURE," TECNA Estudios y Proyectos de Ingeniería S.A., 2013.



	Non regenerative, continuous (usual arrangement: lead/lag)		
Physical absorption	Regenerative, continuous	Physical solvents	Selexol, Rectisol, Purisol, Fluor Solvent, IFPexol, etc.
Physical-chemical absorption	Regenerative, continuous	Physical-chemical solvents	Sulfinol, Ucarsol LE 701, 702 & 703, Flexsorb PS, etc.
Physical adsorption	Regenerative, continuous (adsorption/desorption sequence)	Molecular sieves	Z5A (Zeochem), LNG-3 (UOP), etc.
Permeation	Continuous	Membranes	Separex, Cynara, Z-top, Medal, etc.

Currently membranes can be employed either stand alone or in a hybrid configuration with the dominant amine scrubbing. In fact, in some niche applications, such as offshore platforms treating high-carbon dioxide, membranes are already preferred. As membrane permeance and selectivity increase, membranes are beginning to compete in more mainstream applications. The main characteristics of the two technologies are summarised in Table 13.

Table 13. N	Main characteristics	of technologies for	CO ₂ removal in na	tural gas sweetening

Item		Amines	Membranes
Acid Gas Content at I	nlet	Up to 70% V	Up to 90% V
Typical Acid Gas Con	tent at Outlet	From 2% V down to deep removal	1% V
Typical Gas Flow Rate (MMscfd)		From low to more than 10	From very low to more than 10
Typical Operating ConditionsPressure		Absorber: 5 to 120 bara Regenerator: 1.5 bara	27 to 100 bara
	Temperature	30 to 60°C (absorption)	< 60°C
Typical Hydrocarbon	Losses	Less than 1%	1 stage: 8 - 15%, 2 stages: 2%
Process Turndown	Gas Flow Rate	30%	20%
Main Equipment Materials Requirements		•Contactor •Regeneration System •Flash Drum •Lean/Rich Amine Heat Exchanger •Lean Amine Cooler •Circulation Pumps SS for certain parts (Lean/Rich Heat Exchanger, Reboiler tubes, regeneration System overhead)	 Inlet Pre-Treatment Membrane Skid Recycle Compressor and Coolers (for 2 stages systems) Pre-treatment: CS or SS (high acid gas content). Membrane Skid: CS
Lay Out Requirement	s	High	Low
Services Requirements		Heating MediumPowerChemicals (e.g. antifoam)	 Pre-treatment requirements (e.g. Power, Refrigeration) For 2 stages: Power (for Compression)
Ease of operation		High complexity	Low complexity
Contaminants		Oxygen, Heavy HC (liquid state), Solid particles, Organic acids	Heavy HC, BTEX, Glycols, Amines, Liquid water
Cost Composition Investment		High	Medium
	Operation	Medium	1 stage: Low 2 stages: Medium
Notes		Outlet gas saturated with water	Gas is dehydrated

Membrane systems are preferred for high CO₂ concentration gas streams (enhanced oil recovery, ca. 50% CO₂, and high pressure) and amine units are preferred for relatively low-concentration gas streams. Moreover, membrane systems are also favourable for processing small gas flows (typically for offshore platforms, <6000 Nm³/h) because of their simple flow schemes, while amine units are more complex and require careful, well-monitored operation³. Figure 9 shows a schematic plot illustrating the effect of gas



flow rate and CO_2 concentration in the gas, providing a choice for CO_2 removal technology. This figure should be used with care, as site-specific issue can produce very different results.



Figure 9. Carbon dioxide removal technology competition³³

High pressure operation is the main challenge for natural gas processing with membrane systems. Despite of the numerous advantages of current commercial membranes, these systems are blamed to perform at lower efficiency than amine systems for acid gas removal for a number of reasons such as the presence of contaminants, concentration, polarization, permeability/selectivity trade-off, physical aging and plasticization³⁷.

3.4.1 Membrane plasticization

Plasticization is a phenomenon well-known to the industrial membrane producers, causing a deviation between pure-gas membrane selectivity and the selectivity measured with high-pressure natural gas. The most important plasticizing component in natural gas is CO₂. At the high pressures of natural gas operations, membrane materials absorb 30-50 cm³ of CO₂/cm³ polymer. This is equivalent to 5-10 wt % of carbon dioxide in the polymer; not surprisingly, the membrane materials become plasticized. The absorbed carbon dioxide swells and dilates the polymer, increasing the mobility of the polymer chains. One consequence is a sharp drop in the polymer glass-transition temperature (Tg); another is a decrease in the mobility selectivity (molecular size). The overall result of plasticization is to reduce the membrane selectivity far below the pure-gas values. The magnitude of the effect is dependent on the gas composition and pressure, and it is also related to the material used³³.

Plasticization is always a limited factor for high pressure CO_2 rich gas to be separated with membranes³. Possible strategies to overcome membrane plasticization are crosslinking of membrane material in order to increase the membrane selectivity and fabrication of membranes with enhanced mechanical strength, such as the mixed matrix membranes, by adding inorganic fillers to the polymer matrix³⁹. Another strategy widely used is the pre-treatment to remove aromatics and other heavy hydrocarbons from the gas^{33,37}.

³⁹ W. J, P. D and W. Koros, "Natural gas permeation in polyimide membranes," J. Membr. Sci. , vol. 228, pp. 227-236, 2006.



3.4.2 Gas pre-treatment

Pre-treatment of natural gas feed streams to control the fouling, plasticization, and condensation of hydrocarbons on the membranes is a requirement for all membrane systems. Oil mist and particulates must always be removed, but for CO₂ removal systems, treatment of the gas to control condensation of liquids on the membrane or excessive plasticization of the membrane is also required.

The problem of liquid condensation on the membrane surface is illustrated in Figure 10. This figure shows two natural gas phase envelope curves. At high temperatures, the natural gas mixture exists as a single phase. However, when the gas is cooled, heavy hydrocarbons in the gas will reach their saturation values and condensation will occur. The dew point is dependent on the pressure and the concentration of heavy hydrocarbons in the gas mixture. When the gas is processed by a membrane, CO₂ and some CH₄ is removed in the permeate. Because membranes are relatively impermeable to heavier hydrocarbons, these components are retained and concentrated in the residue gas. This increase in heavy hydrocarbon concentration in the gas causes the phase envelope to shift to higher temperatures.



Figure 10. Graph showing the change in the phase envelope of CO₂-containing natural gas during processing of the gas by a CO₂-selective membrane³³

A solution to the condensation problem previously described is to heat the feed gas sufficiently so that the residue gas, even when cooled by Joule-Thompson expansion, does not enter the phase envelope. Nonetheless, these high temperatures reduce the selectivity of the membrane. A second solution is to remove some of the most condensable components in the gas to change the shape of the phase envelope before sending the gas to the membrane unit. This could be done using glycol absorption (to remove water), in combination with cooling and condensation (to remove C_4 + hydrocarbons)³³.

Two possible pretreatment trains for a carbon dioxide membrane separation plant are illustrated in Figure 11. The design labelled "maximum pretreatment" would be used for a gas that contains high levels of CO_2 and a high concentration of heavy hydrocarbons. The pretreatment train labeled "minimum pretreatment" would be used for relatively hydrocarbon-lean gas that contains much smaller amounts of CO_2^{33} .





Figure 11. Natural gas pretreatment trains used in front of carbon dioxide membrane separation systems^{33,36}

The lack of implementation of adequate pretreatment is proven to have severe effects of the membrane plants, as several systems were damaged in the past due to the concentration in high levels of contaminants or liquids on the membranes. Now, better plant designs are used to control membrane damage, and today's membranes are also more robust.

3.5 System configurations

3.5.1 Membrane module types

Current membranes used for natural gas separation applications are produced as hollow-fibers or flat sheets packaged as spiral-wound modules. Hollow-fiber modules allow large areas of membrane to be packaged into compact membrane modules, nonetheless, the spiral wound module is having fewer blockages than hollow fiber module³⁷. Natural gas streams contain multiple components, some of which (water, carbon dioxide, C₄+ hydrocarbons, aromatics) degrade and plasticize the membrane. Natural gas streams may also contain entrained oil mist, fine particles, and hydrocarbon vapours that can easily collect on the membrane surface. In addition, the gas is typically treated at relatively high pressures of 30-60 bar. Under these conditions, the generally higher permeances of flat sheet membranes formed as spiral-wound modules can compensate for their higher cost on a cost per m² membrane basis, compared to hollow-fiber modules³³. Currently, both types of membrane modules (spiral and hollow-fiber) are produced by different companies and still it not clear which has the lead³⁶.

One trend that has emerged in commercial gas separation membranes is a move to composite membranes, in which a base anisotropic membrane is used as a highly porous support (to provide the mechanical strength required), and a thin layer of permselective material (typically 0.2-1.0 μ m thick) is deposited onto the support to perform the separation. Hollow-fiber membranes and flat sheet membranes can be made in this composite membrane form. Composite membranes, offer two key advantages over the conventional Loeb-Sourirajan anisotropic membrane, as shown in Figure 12³³.



100 microns

Figure 12. Structure of membranes used in natural gas separation process, hollow-fiber. (A) Anisotropic Loeb-Sourirajan membranes and (B) composite membranes³³

In Loeb-Sourirajan membranes, the porous support layer that provides mechanical strength and the relatively dense surface layer that performs the separation are formed at the same time from the same material. This limits the number of materials that can be used to make the membrane³³. It also means the separation properties are often compromised to make membranes with sufficient mechanical strength. A Loeb-Sourirajan membrane generally uses ~50 g of polymer/(m² membrane), so the material cost of membrane made from these high-cost polymers is in the $42 \text{ €/m^2} - 427 \text{ €/m^2}$ range³³.

Composite membranes consist of a microporous support layer coated with one or more thin layers of a different polymer that performs the separation. Because the separation function and the mechanical support function are separated, each can be optimized separately, and the polymer best suited for each function can be used. Composite membranes generally use a dense layer of polymer only 0.2-0.5 μ m thick, so less than one gram of polymer/m² of the high-performance material is needed for a comparable separation. The cost of this polymer is much more affordable, at $0.85/m^2 - 0.85/m^2$. The microporous support membrane for most natural gas applications can be made from conventional low-cost materials³³. Overall, composite membranes allow high-cost polymer materials to be used economically in the separating layers. Tailor-made polymers with good separating properties often cost as much as 0.85/kg-0.85/kg to synthesize. Table 14 lists the principal current suppliers of membranes for natural gas separation systems.

Supplier	Principal natural gas separation	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 silicone rubber

 Table 14. Principal suppliers of membrane gas separation systems



PRISM (Air Products)	Water	Hollow fiber	Polysulfone

3.5.2 Membrane system configuration

A second emerging trend in commercial membrane separations is a move to larger membrane modules. Natural gas separations operate with high-pressure flammable gases that must be contained in code-tamped heavy steel vessels³³. The impact of the cost of these vessels, flanges, valves, and pipes on the system capital cost is illustrated in Table 15. According to this, it can be seen that the cost of membranes used in gas separation processes is a small fraction of the final membrane skid cost.

Table 15. Typical costs for membranes, membranes of 8 inch-diameter spiral wound and module skid³³

Type of Unit		Cost gas separation (steel vessels and components)	
Membrane	€/m ²	17	
Membrane in spiral wound module	€/m ²	85.38	
Membrane module in a skid	€/m ²	427	

One way to reduce membrane skid cost is to increase the permeance of the membranes, allowing a smaller membrane area to be used to treat the same volume of gas. Increasing the feed gas pressure also reduces the membrane area required, and, hence, skid size, but at the expense of larger compressors (higher capital cost) and increased energy consumption (higher operating cost). A third approach is to develop larger membrane modules and new skid designs. Currently, most modules, both spiral-wound or hollow fiber, are designed to fit in 8-in.-diameter housings. However, 12-in.-diameter spiral-wound modules are now being installed in some units, and some hollow fiber module producers are also beginning to introduce very large modules. These developments, combined with the use of lower-cost module skids, are likely to significantly reduce the cost of future membrane systems and increase their long-term competitiveness³³.

The design of a membrane carbon dioxide removal system will be dependent on the following factors:

- The selectivity and permeances of the membranes used
- The CO₂ concentration of the gas and separation requirements (for other components in the gas)
- The natural gas prices
- The location of the plant (on an offshore platform, the weight, footprint, and simplicity of operation are critical; onshore, total cost is more significant).

Block diagrams of two typical carbon dioxide removal plants that treat natural gas with low CO₂ concentration are illustrated in Figure 13. Both plants are designed to treat 10 MMscfd of gas that contains 10% CO₂. A two-stage membrane system with a CO₂ permeance of 0.3 m³ (STP)/(m²/h bar) and a CO₂/CH₄ selectivity of 40 is reported to be comparable to amine process, and could meet the sales standards (<2% CO₂ in natural gas). A combination of hybrid processes comprising a membrane system for bulk removal of CO₂ from crude natural as feed with an amine unit for final purification to reach the pipeline specification (<2% CO₂) could be the optimal process for natural gas sweetening⁴⁰.

⁴⁰ He X. (2015) Membranes for Natural Gas Sweetening. In: Drioli E., Giorno L. (eds) Encyclopedia of Membranes. Springer, Berlin, Heidelberg.



3.5.2.1 One-stage and two-stage unit

One-stage units, which are simple, contain no rotating equipment and require minimal maintenance, are preferred for very small gas flows. In such plants, methane loss to the permeate is often 10%-15%. If there is no fuel use for this gas, it must be flared, which represents a significant revenue loss. For gas wells that produce 1 MMscfd, one-stage membrane units, with their low capital and operating costs, may make sense economically. As the natural gas stream increases in size, the methane loss from a one-stage system and the resultant loss in revenue soon make the choice of a one-stage system unattractive. Therefore, usually, the permeate gas is recompressed and passed through a second membrane stage. These second stage processes are more expensive, because a large compressor is required to compress the permeate gas. However, the loss of methane with the fuel gas is significantly reduced³³.



Figure 13. Flow scheme of one-stage (up) and two-stage membrane separation modules to remove CO₂ from natural gas (P/ICO₂=100 GPU; P/ICH4=5 GPU)³³

3.5.2.2 Three-stage unit

This process design is commonly used to treat a high CO₂ concentrated gas on offshore platforms. The design combines a one-stage and a two-stage system. As shown in Figure 14, the 50 MMscfd of feed gas that contains 30% CO₂ is sent, after pre-treatment, to two sets of membrane modules. The first set of modules reduces the CO₂ concentration from 30% to 15%, producing a permeate stream that contains 82% CO₂. This permeate gas is vented or reinjected. The second set of modules reduces the carbon dioxide concentration in the residue gas from 15% CO₂ to 8% CO₂; it contains too much hydrocarbon to be vented or burned, so it is compressed and passed through a second membrane stage to produce a second stage permeate that contains 93% CO₂ that can be vented. The second stage residue that contains 30% CO₂ is recycled to the front of the system³³. The product gas from the combined system contains 8% carbon dioxide. This is well above the gas grid specification but is low enough to control the corrosion of dry gas, and it allows the gas to be piped to shore, where the remaining carbon dioxide can be removed.



Figure 14. Combination two-stage and one-stage membrane system to remove CO₂ from high concentration gas on Offshore platforms³³

This methane loss of $\sim 7\%$ could be reduced by increasing the size of the second-stage compressor and membrane unit to treat some of the first stage permeate. Installing this larger equipment would be worthwhile at most onshore plants, and its installation could reduce methane loss to 3%-4%. However, offshore, the increase in weight, footprint, power consumption, and other cost-of-plant factors, may not be offset by the value of extra gas recovered.

3.5.2.3 Combined dehydration and sweetening unit

A designed hybrid membrane systems for integrated natural gas dehydration and sweetening using both water-selective and CO₂-selective membranes are feasible to achieve the separation requirement with hydrocarbon (HC) purity of >97.5 mol% and dew point of <-40 °C, but HC loss has been reported to be relatively high. The process operating parameters such as interstage feed pressure and permeate pressure of the membrane units were found to have great effects on membrane system performance. The optimal pressure ratio of the 2nd-stage membrane unit is identified as 15, while the 3rd-stage permeate pressure around 2 bar is required to maintain a relatively low natural gas processing cost. Pursuing a very low-pressure ratio will increase membrane unit cost dramatically, and thus increase the total capital cost. The lowest specific cost of 2.55×10^{-3} \$/m³ purified natural gas was theoretically estimated without captured CO₂, however, this will influence CO₂ emissions. Moreover, novel dehydration membranes with higher water/HC selectivity at high pressure Should be developed in the future, and advanced membranes with high performance for high pressure CO₂/CH₄ separation is also required. Nevertheless, process design and optimization should be well considered to achieve a high separation performance for the whole membrane system²⁴.



Figure 15. Process flow diagram of a hybrid membrane system for natural gas dehydration and sweetening²⁴

3.6 Membrane materials

Key requirements for natural gas sweetening are permeability and big module size, in comparison with e.g. biogas upgrading where the focus is mostly on the selectivity of the membranes. This is due to the fact that biogas and natural gas have different chemical composition (with biogas to contain more contaminants), flow rates (for biogas upgrading ranges between ~100-5000 Nm³/h while for natural gas between 20.000-200.000 Nm³/h), and operate under different conditions (low pressures for biogas, high pressures up to 100bars for natural gas). To achieve high permeance and selectivity, the type of membranes taken into consideration, are those mainly for CO₂ removal. These include:

- polymeric membranes,
- inorganic membranes,
- mixed-matrix membranes and
- carbon molecular sieve membranes.

To this day, only polymeric membranes are commercially available for natural gas sweeting application and in fact, only three polymeric types are applied for CO₂ removal: cellulose acetate, polyimides and perfluoro-polymers⁴¹. However, they have limited performance and are susceptible to plasticization either by CO₂ or heavy hydrocarbon components in the feed gas that might jeopardize its long-term market position. The novel, high performance composite FSC membranes have also shown great potential for CO₂/CH₄ separation³. From all types of membranes, asymmetric hollow-fibers are the ones preferred as they enhance productivity and reduce the cost of membranes in gas separation technology¹⁵. Hollow fiber membranes have surface area to volume ratios over 30 to 50 times than spiral wound membranes, that is, up to 10,000 m²/m³. The small dimension of hollow fibers provides the membrane the capability of withstanding high feeding pressures. They can reduce the effective separating layer to a thin integral "skin" on the outer layer of the fibers. The thickness of this skin layer is critical in natural gas separation as a thinner skin offers a higher separation productivity.

⁴¹ Scholes, Colin & Stevens, Geoff & Kentish, Sandra. (2012). Membrane gas separation applications in natural gas processing. Fuel. 96. 15–28.

Component to be pretreated	Category of preferred polymer material	Typical polymer used	Typical selectivity over methane*(%)
CO ₂	Glassy	Cellulose acetate, polyimide, perfluoropolymer	10-20
H ₂ S	Rubbery	Ether-amide block co-polymer	20-30
N ₂	Glassy	Perfluoropolymer	2-3
	Rubbery	Silocone rubber	0,3
Water	Rubbery or glassy	Several	>200
C3+ hydrocarbons	Rubbery	Solicone rubber	5-20

Table 16. Current commercial membrane materials and selectivities for separation of impurities from natural gas⁸

*Selectivities are typical of those measured with high-pressure natural gas

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3.6.1 Experimental Study Cases - PEBA membrane combinations

Separation of CO₂ from other gases using PEBAX based membranes has attracted great attention recently. PEBA is considered a high-performance copolymer in sweetening of low-quality natural gas. This block copolymer contains soft polyether (PE) blocks that provide high permeability and hard polyamide (PA) blocks that give mechanical strength. Its low permeability indicates the need for a permeable support (coat) that is also of sufficient mechanical strength in order to make it an economically attractive solution for the industry. For this reason, various inorganic and organic filler are considered, such as PEG, SiO2, POSS, SAPO-34, MWCNT, ZIF-8, ZIF-7, zeolite X and zeolite 4A have been incorporated into PEBAX matrix^{42,43}.

3.6.1.1 Sour gas transport in poly(ether-b-amide) membranes for natural gas separations

This study examined the impact of the feed composition on the gas transport properties of PEBA (Pebax®) membranes. The results show the importance of membrane stability: CO_2/CH_4 of selectivity in various feed gas content (mixed, more realistic feed) and pressure. When exposed to a 20% H₂S-containing feed, Pebax® 1074 and 1657 retained the highest selectivity of 12.0–12.8 for CO_2/CH_4 and 79.9–80.6 for H₂S/CH₄ at 55bar. To ensure industrial relevance, future membrane research must be cognizant of the intended application operating conditions and how they will affect membrane performance⁴⁴.

3.6.1.2 PEBAX-1074/ZnO nanocomposite with improved CO₂ separation performance

Polymeric nanoparticle membranes (PNMs) are fabricated in order to overcome the upper-limit boundary. In this study, PEBAX-1074 was considered as a base polymer matrix for fabricating polymeric nanocomposite membranes via ZnO nanoparticles. ZnO is cheap and has high surface-to-volume ratio and can increase the thermal stability of PEBAX. With 8% ZnO was achieved the best gas permeation: CO_2 permeability of 152 Barrer, CH₄ of 11.26 Barrer, N₂ of 2.45 Barrer, while the ideal selectivity* are 13.52 for CO_2/CH_4 and 62.15 for $CO_2/N_2^{43,45}$.

 ⁴² M. Elyasi, M. Momeni, R. Ghalandarzedeh and B. A. e. al, "Fabrication of PEBA/PSF composite membrane for natural gas sweetening," in 4th International Conference on Recent Innovations in Chemistry and Chemical Engineering, Tehran, Iran, 2017.
 ⁴³ N. Azizi, T. Mohammadi and R. Behbahani Mosayebi, "Synthesis of a PEBAX-1074/ZnO nanocomposite membrane with improved CO2 separation performance," Journal of Energy Chemistry, vol. 26, no. 3, pp. 454-465, 2017.

⁴⁴ D. J. Harrigan, J. Yang, B. J. Sundell, L. I. J. A., J. T. O'Brien and M. L. Ostraat, "Sour gas transport in poly(ether-b-amide) membranes for natural gas separations," Journal of Membrane Science, vol. 595, 2020.

⁴⁵ J. Sun and a. al., "MOF-801 incorporated PEBA mixed-matrix composite membranes for CO2 capture," Separation and Purification Technology, vol. 217, pp. 229-239, 2019.



*Ideal gas selectivity of a membrane is defined as the ratio of the permeability of two pure gases, measured separately under the same condition.

3.6.1.3 Fabrication of PEBA/PSF composite membrane for natural gas sweetening

In this study, PEBA was coated on nanostructure PSF (polysulfone) support to prepare PEBA/PSF composite. PEBA film was coated as thin as possible on top of a highly permeable PSF support. So PEBA/PSF composite membrane shows high permeance for CO₂. Moreover, the permeance of CO₂ increases with the increase of transmembrane pressure due to plasticization of the selective layer (for ΔP between 2-8 bar, permeance~50-60 GPU). For PEBA/PSF composite membrane the main transport resistance for gas permeation is mainly from PEBA selective layer, leading to higher permeance for CO₂ and lower permeance for N₂. So with coating a thin and defect-free PEBA film onto a sufficient support can make the membrane economically achievable for the application in industrial natural gas sweetening⁴².

3.6.1.4 Modification of PEBA by PEG

The results of this study showed that the performance enhancement of PEBA copolymers could be done by blending and MMM. The latter enhanced more the selectivity of the membrane. In the case of blending Pebax-1657/CS was reported with the maximum CO₂ permeability of 2884 Barrer and selectivity of 23.2 for CO₂/CH₄. Mixed matrix membranes containing PEO have shown superior performance for separation of CO₂/N₂ and CO₂/CH₄. Pebax-1657/SAPO-34 and Pebax-1074/SAPO-34 membranes showed the highest selectivity for CO₂/N₂ and CO₂/CH₄ have been reported as 137 and 74 respectively. The inclusion of Ionic Liquids (ILs)* into the PEG/PEO-based polymeric membranes can enhance the performance of CO₂ separation but mostly for CO₂/N₂.

Overall, the different type of fabrication of PEO containing membranes for carbon dioxide separation plays a major part in the performance. These methods mainly consisted of the blending of polymers, creating new chemical structures through copolymerization and crosslinking, mixed matrix membranes and using ionic liquids (ILs). Usually, PEO based polymers suffer from weak mechanical properties, therefore creating new chemical structures through copolymerization, crosslinking and mixed matrix structures would lead to membranes with acceptable mechanical strength. The blending of polymers has also produced membranes having high permeabilities for CO₂, with no significant effect on the selectivity of carbon dioxide separation from light gases. However, it was observed that indirect blending gave enhanced selectivities. On the other hand, mix-matrix and ionic liquid seems to give better results. Table 17 presents a collective of higher performance membranes fabricated via indirect, mix-matrix and ionic liquids found in the literature⁴⁶.

Specifically for natural gas separation, the goal for the BIOCOMEM project is to fabricate membranes with performance larger of 100 GPU and selectivity CO₂/CH₄ larger than 50. A list of high-performance membranes found in the literature can be seen in Table 17.

⁴⁶ A. Kargari and S. Razeinia, "State-of-the-art modification of polymeric membranes by PEO and PEG for carbon dioxide separation: A review of the current status and future perspectives," Journal of Industrial and Engineering Chemistry, vol. 84, pp. 1-22, 2020.


Table 17. High performance membranes for CO₂ separation^{46,47}

Selective layer	Support	Feed gas (CH ₄ /CO ₂ /H ₂ S)	Temperature (°C)	Pressure (bar)	Pco2 (barrer)	Pco2 (GPU)	αCO ₂ /N ₂	αCO ₂ /CH ₄	Ref.
Pebax-1657/Matrimid 5218	Indirect blending+PEG				21.7			56,60	46
Pebax-1657/VAc-DBM	Indirect blending+PEG			3	103.35			37.47	
Pebax-1657	Co-polymeric+PEO	Pure	25-30	35	162			64.54	
Pebax-1657/FS	MMM+PEG	Pure	25	35	219			74.50	
Pebax-1657-PEGDME-CNT	MMM+PEG	Pure	20	8	95.14			45	
Pebax-1657/PEG/NaX	MMM+PEG	Pure	20	8	95.14			46	
Pebax-1657/ ZnCo-MOFs	MMM+PEG		25	2	510			56,8	
Pebax-1657/ Fe-BTC	MMM+PEG	Pure	25	3	402.69			215	
Pebax-1657/Ag/[Bmim][BF4]	IL		35	10	180		187,5	61	
PEBAX-1074/ZnO	MMM+PEG		25	3	152.27		62,15	13.52	
PEBAX	ZIF-8 (35% wt)	Pure	25	6	1287			32.30	47
PEBAX 1657	ZIF-8 (8% wt)	Pure	30	2	285			48	
PEBAX 1657 (F.A APTES)	ZIF-8 (40% wt)	Pure	35	5		690		16	
PEBAX 1657		Pure	35	5		310		17	
PZ30T		Pure			344			24.2 0	
IL/PEBAX1657		Pure			152			13.50	
SAPO-34/PEBAX1074		Pure			250			45	
ZIF-8/PEBAX1657		Pure			450			13.80	
PEBAX1074		Pure			165			24.50	
ZIF-8/PEBAX2533		Pure			1287			9	
4A Zeolite/PEBAX1657		Pure			155.7			41.30	
PEBAX1657/CNT/GTA		Pure			210			19	
PEBAX (F.A. APTMS)	ZIF-8	Pure	35	5		610		14.50	
PEBAXSA4033		70.8/27.9/1.3	35	10		84.4		6.50	
PEBAX Mx 1074		70.8/27.9/1.3	35	10		122		12	

⁴⁷ Abolfaz Atash Jameh, Toraj Mohammadi, Omid Bakhtiari, Preparation of PEBAX-1074/modified ZIF-8 nanoparticles mixed matrix membranes for CO2 removal from natural gas, Separation and Purification Technology, Volume 231, 2020,115900

*Ionic liquids (ILs) are the salts that are in liquid form at temperatures below 100 °C and can dissolve organic and inorganic materials. * E_{A} = Functional agent

**F*.*A*.=*Functional agent*

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3.7 Industrial requirements

3.7.1 Pressure categorization to grid

Natural gas exists in three different quality gases: High quality gas (H-gas), Low quality gas (L-gas) and Groningen quality gas (G-gas). The H and L-gases are differenced by the Wobbe index and the amount of nitrogen. Generally, the gas can be injected with different pressures in the gas grid, depending on the network, as seen in Table 18. The pressure therefore can be categorized in high pressure, medium pressure, and low pressure.

Table 18. Categories pressure in different European natural gas networks

Network	Gas	Pressure	Pressure (Netherlands)
HTL (Head Transportation Network)	G-gas and H-gas	usually > 16 bar	> 45 bar(a)
RTL (Regional Transportation Network)	Mostly G-gas	about 4-16 bar	11 – 40,5 bar(a)
RNB (Regional Network Operator)	Mostly G-gas	< 4 bar	9 / 4 / < 4 bar(a)

Country	High pressure (bar)	Medium Pressure (bar)	Low pressure (bar)
France 40-70		3 types: MPC: pressure between 4 and 25 bar MPB: pressure between 0,4 and 4 bar MPA: pressure between 0.05 and 0.4 bar	≤50mbar
Germany	>1	> 0.1 bar $- \le 1$ bar	$\leq 0,1$ bar
Italy	It is the gauge pressure of the gas exceeding 5 bar	It is the gauge pressure of the gas exceeding 0.04 bar and not exceeding 5 bar	It is the gauge pressure of the gas not exceeding 0,04 bar
Netherlands	40 bar to 80 bar. This network is maintained by the TSO. Levels: 40 bar 67 bar	The medium pressure network is maintained by the DSO. P > 200 mbar (high pressure DSO) Levels: 1 bar 2 bar 4 bar 8 bar	The pressure of the low pressure network is smaller than or equal to 200 mbar. The low pressure network is maintained by the DSO. P \leq 200 mbar (low pressure DSO) Levels: 100 mbar 30 mbar
Spain	Up to 4 bar (rel) of maximum operation pressure	From 0.05 up to 4 bar of maximum operation pressure	From 0,05 up to 4 bar of maximum operation pressure

Table 19. Pressure level gas network in different European countries (examples)⁴⁸

*Transmissions system operators (TSO)

*Distributions system operators (DSO)

3.7.2 Other requirements

To qualify a gas, one should consider different indicators, such as the Wobbe index, calorific value, density and specific gravity, methane number and the concentration of hydrogen sulphide, carbon dioxide and oxygen. Other factors that are required to be controlled and monitored include the hydrogen concentration, other hydrocarbon's concentration, water dew point, temperature and pressure. Those type of requirements give important information on which market is the most restricted and, therefore needs a robust membrane system to obtain the higher amount of methane.

⁴⁸ 6th Ceer benchmarking report on the quality of electricity and gas supply, 2016, https://www.ceer.eu/



Table 20. Other requirements natural gas grid network in Europe^{49,50}

	CEN standard	gas quality EN16726:2015	EASEE (EU standard)		Dutch gas grid		
	Н	H- group		Sector	G-gas	H-gas	
Delative density	Min	0.555	0.62				
Relative density	Max	0.7	0.62				
Total sulfur without	Min						
odourant mg/m3	Max	20					
Total sulfur in gas with	Min		-				
odourant mg/m ³	Max	30	30				
HaS+COS mg/m ³	Min		-				
	Max	5	5				
Moreonton sulfur mg/m ³	Min						
wiercaptan sunur ing/in	Max	6					
Overgan mal/mal	Min			RTL& RNB	≤ 0.5	≤ 0.5	
Oxygen mon/mon	Max	10 ppm to 1%	1%	HTL	≤ 0.0005	≤ 0.0005	
CQ: mal/mal	Min	-		RTL& RNB	≤ 10.3 (1)	≤ 2.5	
	Max	2.5% to 4%	2,5%	HTL	< 3	≤ 2.5	
HC dew point °C (up to	Min						
70 bar)	Max	-2	-2				
Water dew point °C (at	Min			RTL&HTL	≤ -8	≤-8	
70 bar)	Max	-8	-8	RNB	\leq -10 (°C at 8 bar(a))		
Mathana numbar	Min	65					
Wietnane number	Max		-7				
Wobbe Index (MJ/Nm ³ at 15°C)		N.A	48.32 - 55.70		43.46 - 44.41	49.9 – 55.7	
Hydrogon (mall/)		N A		RTL& HTL	≤ 0,02	$\leq 0,02$	
riyurogen (mor76)		N.A		RNB	$\leq 0,1$	\le 0,02	
Calorific value					not lower than 1,5 % of average caloric value of the gas that is entered the RNB grid from the RTL/HTL national grid of the last 12 months		
Higher hydrocarbons (mol% PE)					≤ 5	No limit	
Earth gas condensation (mg/m ³ at -3°C)					≤ 80	≤5	
Tomporature (%C)				RTL& HTL	10-30	10 - 30	
				RNB	5-20	10-30	

⁵⁰ https://ec.europa.eu



4 BIOGAS UPGRADING

In recent years, many biogas upgrading technologies have been developed, and their main differences are related to the nature of the operation. These include physical, chemical, and biological differences, their variation in efficiency and operational conditions, as well as investment and maintenance costs. The current technologies include pressure swing adsorption (PSA), physical absorption (water and organic solvent scrubbing), chemical absorption, cryogenic separation, membrane separation and biological methane enrichment²⁷.

4.1 Biogas applications

Biogas is produced from the methanation of biomass and organic wastes from sewage sludge anaerobic digestion, commercial composting, landfills, biomass gasification (thermo-chemical production process), animal farm manure anaerobic co-digestion with energy crops, agro-food industry digestion facilities in both mesophilic (35° C) and thermophilic (55° C) conditions. Raw biogases from anaerobic degradation of sewage sludge, livestock manure, and agro-industrial bio-waste are generally composed of CH₄ (55-70%), and CO₂ (30-45%). Other gases (contaminants) present are N₂ (0-15%), O₂ (0-3%), water (1-5%), hydrocarbons ($0-200 \text{ mg m}^{-3}$), H₂S ($0-10,000 \text{ ppm}_v$), ammonia ($0-100 \text{ ppm}_v$), and siloxanes ($0-41 \text{ mg Si} \text{ m}^{-3}$). Biogas produced from landfills is some complex mixtures, which composed of methane (35-65%), carbon dioxide (15-40%), hydrogen (0-3%), carbon monoxide (0-3%), nitrogen (5-40%), oxygen (0-5%), water (1-5%), halogenated hydrocarbons ($20-200 \text{ ppm}_v \text{ Cl}^-/\text{F}^-$), hydrogen sulphide ($0-100 \text{ ppm}_v$), ammonia ($0-5 \text{ ppm}_v$), volatile organic compound ($0-4500 \text{ mg/m}^3$), and siloxanes ($0-50 \text{ mg Si} \text{ m}^{-3}$). Typical compositions of different types of biogas are comparable with natural gas. The possible impact of contaminants is shown in Table 21^{27} .

As biogas composition does not usually fulfil the national regulations⁵¹, a biogas upgrading process is needed. Biogas upgrade to biomethane aims to remove unwanted impurities to produce biomethane with a methane concentration above 95%, and often (depending on downstream application) a heating value comparable to pure methane (for pipeline injection ~35 MJ/Nm³). This is needed for most applications on the EU market today (injection in the grid and delivery to households and industry or use as a fuel for compressed natural gas vehicles) and requested by national regulations²⁷.

Generally, in the upgrading process, the raw biogas is passed through mechanical filters to remove solid particles. Oxygen is normally completely consumed by the reaction of aerobic microorganisms in the digester. Hydrogen has some restriction or requirements in a ppm level to apply for grid injection or for use as vehicle fuel (e.g. in Europe ~500 ppm). H₂ separation is therefore not necessary. However, it is interesting to mention that membrane are selective to H₂ as well, and in fact, the selectivity H₂/CO₄ is even higher than CO₂/CH₄ theoretically. On the other hand, N₂ in the biogas can be partly eliminated via membranes or low temperature pressure swing absorption (PSA), however this is costly. Nitrogen presence in the biogas means that air has been sucked in, therefore, air should not be allowed inside to limit N₂ in the biogas⁵².

 $^{^{51}}$ The specifications of the biomethane composition are depending on national regulations and in some countries > 95% methane content is required. The lower the CO₂ and N₂ content, the higher is the energy content of the methane and hence higher is the fuel calorific value. From "Biogas upgrading and utilization: Current status and perspectives", DOI:10.1016/j.biotechadv.2018.01.011

⁵² R. Munoz and e. al., "A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading," Rev Environ Sci Biotechnol, vol. 14, p. 727–759, 2015.



 CO_2 is sometimes considered to be a nuisance because of large quantities (10-65%), and is inert in combustion, thus decreasing the biogas calorific value. Therefore, removal of CO_2 is very important for biogas upgrading. The separation of CO_2/CH_4 by membrane is based on CO_2 and CH_4 having different solubility and diffusivity in the membrane. Generally, biogas upgrading consists of two steps. Removal of CO_2 to increase the gas calorific value, and elimination of undesired molecules such as water, H_2S , ammonia, as well as potential TOC (trace organic components) to improve biogas performance. Removal of CO_2 is also necessary to meet Wobbe Index quality and specifications.

Parameters	Unit	Biogas from AD	Landfill gas	North Sea Natural gas	Impact on biogas utilization
Lower heating value	MJ/Nm ³	23	16	40	
-	kWh/Nm ³	6.5	4.4	11	
	MJ/kg	20	12.3	47	
Density	kg/Nm ³	1.1	1.3	0.84	
Relative density		0.9	1.1	0.63	
Wobbe index, upper	MJ/Nm ³	27	18	55	
Methane number		>135	>130	73	
Methane (CH4)	vol%	60–70	35–65	85–92	
Heavy hydrocarbons	vol%	0	0	9	
Water vapour (H ₂ O)	vol%	1–5	1–5		Corrosion in compressors, gas storage tanks and engines due to reaction with H ₂ S, NH ₃ , CO ₂ to form acids
Hydrogen	vol%	0	0	0	
Carbon dioxide (CO2)	vol%	30-40	15-40	0.2–1.5	Decreasing calorific value, anti-knock properties of engines and corrosion
Nitrogen (N ₂)	vol%	0-0.5	15	0.3–1.0	Decreasing calorific value, anti-knock properties of engines and corrosion
Oxygen (O ₂)	vol%	0	1		Corrosion, fooling in cavern storage, risk of explosion
Hydrogen sulphide (H2S)	ppm	0–4000	0–100	1.1–5.9	Corrosion, catalytic converter poison, emission, and health hazards. SO ₂ , SO ₃ are formed.
Ammonia (NH ₃)	ppm	100	5	0	Emission, anti-knock properties of engines and corrosion when dissolved
Total chlorine as Cl [−]	mg/mm ³	0-5	20–200		Corrosion in engines

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Table 21.	rarameters and	composition of	of gases from	unterent origins,	impurities, and	their consequences

4.2 Market Size

The number of biogas upgrading plants in Europe has followed an upward trend over the last years, reaching 580 plants in 2019 accounting for an increase of 21% compared with 480 plants in 2016 and 12.4% reporting 508 plants by December 2017 (see Figure 16A). The number of biogas upgrading plants located in Germany, UK, Sweden and The Netherland together represents 70% of the market operation, conditioning diverse volume capacities of raw biogas (70-6000 Nm³/h) and producing between 70 Nm³/h to 3000 Nm³/h of biomethane. This membrane based technology is becoming the preferred upgrading technology in EU, led by UK, The Netherlands and France (see Figure 16B), with the 28% of biogas upgrading plants using membrane technology in 2019.





Figure 16. Overview distribution Biogas upgrading plants (A) and Biogas upgrading technologies (B) in Europe⁵³



Figure 17. Development of biogas upgrading technologies⁵⁴

Figure 17 shows that membrane is one of the favored upgrading technologies worldwide, nonetheless, water scrubbing, chemical scrubbing and PSA still depicts significative presence in the market. Main suppliers such as Malmberg Hitachi, Carbotech and Greenlane, use different technologies than membrane⁵³. Since the first market introduction of high selective membrane performance in Poundbury (2013), membrane technology is increasing its market share, overcoming PSA in number of plants. Estimating an annual growth rate of 13% for upgrading plants using membranes, will have the 36% of the market in 2025, the 67% in 2030.

⁵³ I. Nobre, "Biomethane Market Overview," DMT, Joure, The Netherlands, 2019.

⁵⁴ I. Bioenergy, "Energy technology Network," International Energy Agency, 37.



4.3 System providers

Table 22 provides with a list highlighting the top 10 membrane system providers for biogas upgrading.

System Provider	Technology used
DMT	Evonik Sepuran membrane
Air Liquide	Medal membrane and PoroGen membrane (polymide)
Prodeval	Evonik Sepuran membrane
Pentair	Water scrubbing, membrane separation
HoSt	Evonik membrane
Envitec	Sepuran Green modules (Evonik)
Hitachi	Evonik Sepuran membrane
Unison/	Membrane CO ₂ removal
BioCNG	
Axiom	Membrane (polymide)

Table 22. Biogas upgrading membrane system providers

4.4 Technology overview for biogas upgrading

 CO_2 removal from biogas at industrial scale is nowadays performed by physical/chemical technologies based on their high degree of maturity and commercial availability, while the potential of biotechnologies has been assessed only at lab or pilot scale. Membrane separation is particularly appealing for biogas upgrading due to its lower energy consumption, good selectivity, easily engineered modules, and therefore lower costs⁸. High CH₄ recovery efficiency can be reached (>99%), while pure CO₂ can be obtained. The main disadvantage of membrane separation is that multiple steps are required to reach high purity. As it can be seen in Table 23, it is reported that there is no general significant difference in neither investment cost nor energy demand between the different biogas upgrading techniques other than the amine scrubber requiring less electricity but more heat than the other techniques. It is therefore more important to consider other aspects such as necessity to pre- or post-treat depending on the raw material quality and product gas standards⁵⁵.

Table 23. Comparison and evaluation of the costs of different biogas upgrading technologies⁸

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	4-14
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 (nonhazardous)	amine solution (hazardous, corrosive)	activated carbon (nonhazardous)	-
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	10100	9500	9500	10400	7300-7600
$\left[\frac{\epsilon}{(m^3/h)}\right]$ biomethane]	5500	5000	5000	5400	4700-4900
for 100 m ³ /h	3500	3500	3500	3700	3500-3700
for 250 m ³ /h					
for 500 m ³ /h					
Typical operational costs	14.0	13.8	14.4	12.8	10.8-15.8
[ct€/m ³ biomethane]	10.3	10.2	12.0	10.1	7.7-11.6
for 100 m ³ /h	9.1	9.0	11.2	9.2	6.5-10.1
for 250 m ³ /h					
for 500 m ³ /h					

Methane slip is an important parameter in biogas upgrading process indicating the methane lost in the process, thus product loss. The methane slip can be influenced through both process optimization and process design and thereof there is a trade-off between methane slip and investment or operation cost. The methane slip for the biogas upgrading techniques discussed in this report are summarized in Table 24. The numbers presented in this table reflect on what is achievable with the different techniques. However, in some cases, extra investment packages are needed to reach the lowest reported methane slip⁵⁵.

Т	able	24.	Methane	slip fo	r different	biogas	upgrading	techniques ⁵⁵

	Methane slip*
Water scrubber	1%
Organic physical scrubber	0.5-2%
Amine scrubber	<0.1%
PSA	1-1.5%
Membrane separation	0.5%
	1 1

*The methane slip is not referring to the methane concentration in a stream released to the atmosphere such as the stripper air in a water or organic physical scrubber and do neither reflect any concentrations of methane in side streams in other upgrading techniques such as membrane separation or cryogenic upgrading

The composition of biogas produced in anaerobic digestion depends on the substrate used in the digester. When choosing a suitable technique for biogas upgrading, it is therefore important to also consider how different compounds present in the biogas affect the process, the product gas as well as possible need for treatment of other streams such as waste gas or process water. The aspects regarding requirements of biogas quality are summarized in Table 18. We have chosen not to include water in this table due to the fact that biomethane drying is a standard operation in biogas upgrading with techniques which do not produce dry biomethane and this is therefore in our opinion not considered a post treatment but rather a part of biogas upgrading. It is, however, important to remember that biomethane drying is required after upgrading with water scrubbers, amine scrubbers and in some cases organic physical scrubbers, while the biomethane produced with membrane separation and PSA is dry enough to be used directly

4.4.1 Membrane separation

Membrane technology for biogas upgrading is based on gas dissolution and diffusion into polymer materials (membranes) or in other words, based on the principle of selective permeation of biogas components through a semi-permeable membrane⁵⁶. When a differential pressure is applied on opposing sides of a polymer dense film, gas transport across the dense film (permeation) occurs. The gas permeation rate is

⁵⁵ https://energiforskmedia.blob.core.windows.net/media/22326/biogas-upgrading-technical-review-energiforskrapport-2016-275.pdf

⁵⁶ F. Bauer, "Biogas upgrading – Review of commercial technologies," in SGC Rapport 2013:270, Malmö, Sweden., 2013.

Bi@	6	****	D2.2 Industrial membrane requirements	Proj. Ref.: Doc. Ref.: DLR-WPL-3	BIOCOMEM-887075 BIOCOMEM-WP2-D2.2- 80112020-v01.pdf
Mem	* BIO-BASED NDUSTRIES * * Public-Private Partnership	* * * * * *	-	Date: Page Nº:	03/11/2020 45 of 74

controlled by the solubility coefficient and diffusion coefficient of the gas-membrane system^{57,58}. Permeability properties of the membranes can be based on gas–gas separation (gas phase on both side of the membranes) or gas–liquid separation (liquid absorbs the H₂S and CO₂ molecules diffusing through the membranes). The gas–gas separation-based process works at high pressure (greater than 20–40 bar), or at lower pressures of 8–10 bar, resulting in 92–97% methane production. Conventional membranes for biogas upgrading retain CH₄ and N₂, and facilitate the preferential permeation of O₂, H₂O, CO₂ and H₂S, with CO₂/CH₄ selectivity factors of up to 1000/1.

Regarding the matter of material selection, typically polymeric materials such as cellulose acetate are preferred over non-polymeric for the manufacture of biogas separating membranes due to their lower cost, easy manufacture, stability at high pressures and easy scalability⁵².

4.4.2 Pressure swing adsorption

Along with amine and water scrubbing, pressure swing adsorption (PSA) is a widely employed biotechnology for biogas upgrading (23% market share by $2013)^{59}$. Several companies develop and commercialize this technology including Carbotech, Acrona, Cirmac, Gasrec, Xebec Inc and Guild Associates. Small scale plants (flowrate of 10 m³/hour of biogas) are in operation, but this technology is also available for much higher flowrates (10000 m³/hour of biogas)⁶⁰.



Figure 18. Pressure swing adsorption flow diagram for biogas upgrading⁶¹

In PSA processes, biogas is compressed to a pressure between 4-10 bar and is fed to a vessel (column) where is putted in contact with a material (adsorbent) that will selectively retain CO₂. The adsorbent is a porous solid, normally with high surface area. Most of the adsorbents employed in the commercial processes are carbon molecular sieves (CMS) but also activated carbons, zeolites and other materials

⁵⁷ A. W. A. Petersson, "Biogas upgrading technology-developments and innovations," IEA Bioenergy. Task 37: Energy from biogas and landfill gas, IEA, 2009.

⁵⁸ N. G. S. I. J. I. Huertas, Mass transfer in chemical engineering, Intech. pp. 133-135., 2011.

⁵⁹ Bauer, F., Persson, T., Hulteberg, C., & amp; Tamm, D. (2013, July 11). Biogas upgrading – technology overview, comparison and perspectives for the future.

 ⁶⁰ C. A. Grande, 2010. Biogas Upgrading by Pressure Swing Adsorption. Biofuel's Engineering Process Technology.
 ⁶¹ "https://americanbiogascouncil.org/processing-psa/"



(titanosilicates) are employed. The purified CH_4 is recovered at the top of the column with a very small pressure drop. After certain time, the adsorbent is saturated with CO_2 , and the column needs to be regenerated by reducing the pressure (normally to vacuum for biogas upgrading). The adsorption of H_2S is normally irreversible in the adsorbents and thus a process to eliminate this gas should be placed before the PSA. Alternatively, depending on the choice of the adsorbent, the humidity contained in the biogas stream can be removed together with CO_2 in the same unit. Multi-column arrays are employed to emulate a continuous process⁶⁰.

4.5 Membrane system configuration

Membrane separation is commercialized either in high pressure gas–gas modules or low-pressure gas–liquid modules⁵⁶. Biogas is pressurized at 20–40 bars in gas–gas systems (although some commercial units also operate in the 6–20 bar range) resulting in a CH_4 rich retentate and a CO_2 rich permeate containing methane and trace levels of H_2S at atmospheric pressure (or negative pressures to increase the purity of the biomethane over 97%).

Gas–gas units are manufactured under different configurations: single pass membrane unit or multiple stage membrane units with internal recirculation of permeates and retentates (Figure 19). On the other hand, gas–liquid systems are operated at (near) atmospheric pressure (with the associated reduction in construction costs) with biogas and a CO₂-liquid absorbent separated by a micro porous hydrophobic membrane. Both fluids flow under counter current mode⁵².



Figure 19. Biogas upgrading by membrane separation. Different configurations of gas-gas units: I single pass membrane unit, II multiple stage membrane units with internal recirculation of permeate and III internal recirculation of retentates⁵²

Table 23 shows that membrane technology presents several advantages. For example, it has the possibility to adjust the plant layout to local particularities like low demand of electric energy, low investment and operating costs. The lower methane recovery (80%) could be improved to 99.5% using multiple membrane steps and multiple compressors or efficient membrane configurations. It is also clear that both investment and operational costs are lower for membrane separation processes¹⁸.

The investment costs of gas–gas membrane units rapidly increase from $\notin 2500$ for design flow rates of 400 Nm³/h to $\notin 6000$ when scaling down the process to 100 Nm³/h. Remaining approximately constant at $\notin 2000$ for plants with capacities over 1000 Nm³/h. The operating costs of this technology are mainly determined by membrane replacement (5–10 years lifetime), biogas compression cost (0.2–0.38 kWh/Nm³) and the

Bi@			D2.2	Proj. Ref.: Doc. Ref.:	BIOCOMEM-887075 BIOCOMEM-WP2-D2.2-
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cost associated to biogas pre-treatment (activated carbon replacement plus energy for condensation)⁵². Costs in the range of $0.13-0.22 \text{ €/Nm}^3$ are typically reported in literature. Membrane-based upgrading exhibits slightly higher maintenance cost (3–4% of the initial investment costs) compared to their physical chemical counterparts $(2-3\%)^{52,56}$.

One of the big advantages in pre-combustion gas-gas separation, is that the CO₂ separation process consumes much less energy than in other processes because it takes place in a smaller reaction volume and at lower volumetric flow rates, elevated pressure and higher component concentration. The higher concentrations make the capture process far less energy-intensive, therefore, pre-combustion carbon capture is intended to be a lot more cost-effective than post-combustion capture⁴. Additionally, no regeneration energy is required, in general the process can be done in a simple modular system and no waste streams are obtained. To the contrary, avoiding membrane plugging by impurities in the gas stream and preventing membrane wetting are the major technical challenges.

4.5.1 Single step gas permeation processes

In the single step gas permeation plants, methane loss can reach 10-15% on the permeate side. If the application is not fuel use, it must be flared leading to revenue loss. Another option would be to couple the single membrane module with a partial permeate recycling stream. CH_4 recovery increases substantially using this process, nevertheless, CH_4 recovery cannot reach more than 95% while a purity of 96% is necessary for grid injection. Furthermore, the flow rate passing through the compressor increases because of partial recycling, and therefore, the energy for driving the separation process increases²⁷.



Figure 20. Single stage membrane-based biogas upgrading process using feed compression. (Left) the permeate flows to the ambient. (Right) the permeate is partially recycled to enhance the CH4 recovery. 260x91mm (300 x 300 DPI)²⁷

4.5.2 Two-step gas permeation processes

In order to improve CH₄ recovery and simultaneously get CH₄ purity, scientists applied various membrane modules in the upgrading system. Four different two-stage upgrading processes are depicted in Figure 21. Process (a) only needs one compressor and recycles the permeate of the second step. Process (b), which was investigated by Deng and Hagg²⁷, needs two compressors and recycles the retentate of the second step. In process (c), which is related to process (b), two compressors are needed and the retentate of the second step is mixed with the one coming from the first step. In process (d) the feed gas is used as a sweep gas on the permeate side of the second module. Process (d) configuration is similar to process (a). When the CO₂ mole fraction in the second module permeate is higher than that of the feed stream, the sweep stream is applied as to decrease the CO₂ mole fraction on the permeate side of the second module. Here, only one compressor is required.





Figure 21. Two stage processes for biogas upgrading. 189x100mm (300 x 300 DPI)²⁷

Deng and Hagg evaluated CH₄ recovery, specific energy, specific membrane area, specific upgrading costs of single stage and three two-stage processes. The results are shown in Table 25. It is seen that process (b) has the lowest upgrading costs, as well as the highest CH₄ recovery and module specific membrane area and specific energy with 66.67 GPU of CO₂ permeability and 2.08 GPU of CH₄ permeability.

 Table 25. Various gas permeation upgrading processes are compared in terms of energy demand, CH4 recovery, required membrane area, and specific upgrading cost⁶²

Process	CH4 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

4.5.3 Three-step gas permeation processes

Three-step biogas upgrading process is similar to process (d) in Figure 21. Depending on the characteristics of the biogas, as well as on the desired quality of the CH₄ product, different configurations can be considered. Configurations that include a vacuum blower, increase the purity of the outlet, work with higher volumes but also increasing the maintenance costs. When comparing stages required, the higher the amount of stages the lower the methane slip. However, reducing the amount of stages also reduced the amount of membranes ($\approx 40\%$) and therefore the CAPEX²⁷.

⁶² K. Vanherck and e. al., "Crosslinking polyimides for membrane applications: A review," Progress in Polymer Science, vol. 38, p. 874–896, 2010.





Figure 22. Different configuration modules for 3-stage membrane separation

In Figure 22(a) the retentate from the 1st module is sent to module 2, while the permeate stream is sent to module 3. In (b), the retentate stage with permeate return from the 2^{nd} stage and permeate stage from module 2 is recompressed and recycled to module 1. Figure (c) describes a similar exemplary interconnection of several membrane modules but without compression of permeate stream from module 1 and Figure (d) shows unpressurized raw biogas mixed with the permeate of module 3 and sent to module 2 on the permeate side as to dilute the CO₂ concentration on the permeate stream of module 2.

4.6 Membrane materials

Most of the membrane materials used today for gas separation are organic polymers. Many polymers can be easily processed into high surface area modules membranes giving reasonable separation property^{63,64}. The main polymers used are polycarbonate (PC), cellulose acetate (CA), polyesters (PE), polysulfone (PSf), polyimide (PI), polyetherimide (PEI) and polypyrrolones. Cellulose acetate, polysulfone and polyimide are used for industrial level utilization.

4.6.1 Experimental Study Cases - PEBA membrane combinations

4.6.1.1 Graphene/PEBA Membranes for CO₂/CH₄ Selectivity

In the present research, the authors introduce novel Graphene/PEBA nanocomposite membranes that were first prepared to improve carbon dioxide permeability and CO_2/CH_4 selectivity. The extrusion process in presence of paraffin liquid was employed to produce GA/PEBA granules with uniform dispersion. The results show that only the addition of 0.4 wt.% of graphene could enhance the permeability of CO_2 and CH_4

⁶³ C. Li and e. al., "Engineered Transport in Microporous Materials and Membranes for Clean Energy Technologies," Advance Materials, vol. 30, pp. 1-33, 2018.

⁶⁴ A. L. Khan and e. al., "SPEEK and functionalized mesoporous MCM-41 mixed matrix membranes," Journal of Materials Chemistry, vol. 22, p. 20057–20064, 2012.



gases effectively, which indicates great economic effects. The highest Carbon Dioxide permeability of 387 Barrer and CO_2/CH_4 selectivity of 32 was occurring at the optimal graphene loading of 0.4 wt.% at 55°C⁶⁵.

4.6.1.2 MOF-801 incorporated PEBA mixed-matrix composite membranes for CO₂ capture

This reference reports a novel mixed-matrix composite membrane with enhanced CO_2/N_2 separation performance by combining MOF-801 filler with PEBA polymer. The synthesized MOF-801 nanocrystals exhibit excellent CO₂ preferential adsorption toward N₂ and good interfacial adhesion to the PEBA matrix, thereby significantly enhancing the CO₂ permeance and CO₂/N₂ selectivity of pure PEBA membrane. The CO₂ permeance of the optimized 7.5 wt% MOF-801/PEBA membrane reached 22.4 GPU, which is 75% higher than the pristine PEBA membrane, meanwhile with 43% higher CO₂/N₂ selectivity. Sorption diffusion analysis confirms that the incorporation of porous CO₂-philic MOF-801 nanocrystals contributes to the enhanced gas separation performance in the MOF-801/PEBA mixed-matrix membrane. Compared with other fillers reported in literature, MOF-801 exhibits a high efficiency for simultaneous enhancing permeance and selectivity for CO₂/N₂ separation, which could be a potential candidate for membrane CO₂ capture application⁶⁶.

4.6.1.3 Supported PEBA-zeolite 13X nano-composite membranes

This research has proved that tri-layer composite membranes increase the strength and permeability of the membranes. The addition of nano-zeolite 13X (with a regular distribution of pores and a large specific surface area) significantly improved both CO_2/N_2 and CO_2/CH_4 selectivity and CO_2 permeability parameters⁶⁷.

4.6.1.4 Magnetic nanoFe₂O₃ – incorporated PEBA membranes for CO₂/CH₄ and CO₂/N₂ separation

Novel PEBA/Fe₂O₃ magnetic MMMs, including different loadings of Fe₂O₃ NPs and PEBA polymers as continuous phases, were fabricated to improve CO₂ separation from light gases such as CH₄ and N₂. A PEBA 0.5 wt% Fe₂O₃ membrane showed higher CO₂ permeability than the pure PEBA membrane under the same conditions, although the best pure gas separation performance of the PEBA/Fe₂O₃ magnetic membranes corresponded to 1.5 wt% loading (CO₂ permeability = 165.6 Barrer, CO₂/CH₄ selectivity = 55.95 and a CO₂/N₂ selectivity = 157.25 at 14 bar).

The incorporation of magnetic Fe_2O_3 NPs and attraction of CO_2 gas into polymer matrix leading to higher permeability, simultaneously confirmed a facilitated transport effect caused by fabrication of MMMs. Such NPs with a magnetic property may have an excellent potential in the novel design of magnetic MMMs with higher gas separation performance⁶⁸.

⁶⁵ S. Yousef and e. al., "A New Industrial Technology for Mass Production of Graphene/PEBA Membranes for CO2/CH4 Selectivity with High Dispersion, Thermal and Mechanical Performance," Polymers - MDPI, vol. 12, pp. 1-5, 2020.

⁶⁶ J. Sun and a. al., "MOF-801 incorporated PEBA mixed-matrix composite membranes for CO2 capture," Separation and Purification Technology, vol. 217, pp. 229-239, 2019.

⁶⁷ M. Asghari and e. al., "Supported PEBA-zeolite 13X nano-composite membranes for gas separation: Preparation, characterization and molecular dynamics simulation," Chemical Engineering Science , vol. 187 , p. 67–78, 2018

⁶⁸ H. R. Harami and e. al., "Magnetic nanoFe2O3 – incorporated PEBA membranes for CO2/CH4 and CO2/N2 separation: experimental study and grand canonical Monte Carlo and molecular dynamics simulations," Greenhouse Science and Technology, vol. 9, p. 306–330, 2017.



4.6.1.5 UiO-66-polyether block amide mixed matrix membranes for CO₂ separation

In summary, this reference reports the design and fabrication of UiO-66 based metal-organic frameworks-PEBA mixed matrix membranes. Compared with UiO-66, UiO-66-NH₂ showed enhanced MOF polymer interactions, which led to excellent dispersibility in polymer matrix. Moreover, stronger affinity with CO₂ molecules was realized after functionalized by amine groups. The gas permeation behaviours of the asprepared membranes were also investigated. The results showed that both of the UiO-66-PEBA and UiO-66-NH₂-PEBA mixed matrix membranes showed significantly improved CO₂ separation performance than that of pure polymer membrane. However, UiO-66-NH₂-PEBA membranes possessed higher CO₂/N₂ selectivity and slightly lower CO₂ permeability than those of UiO-66-NH₂-PEBA exhibited high and stable CO₂/N₂ separation performance (CO₂ permeability: 130 Barrer, CO₂/N₂ selectivity: 72 in humid state, transcending the upper bound for state-of-the-art polymeric membranes. This work demonstrated that UiO-66 based metal-organic frameworks are promising materials for developing mixed matrix membranes, which offer promising potential for CO₂ capture. Compilation of PEBA membrane performances, considering BIOCOMEM's first goal to produce at pilot scale new biobased PEBA co-polymers. For upgrading of Biogas: P_{CO2} (STP) > 60 GPU and CO₂/CH₄ selectivity >50.

Compilation of PEBA membrane performances, considering BIOCOMEM's first goal to produce at pilot scale new biobased PEBA co-polymers. For upgrading of Biogas: P_{CO2} (STP) > 60 GPU and CO_2/CH_4 selectivity >50.

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Selective layer	Gas inlet	Support	Temperature (°C)	Pressure (bar)	PCO ₂ (Barrer)	PCO ₂ (GPU)	aCO ₂ /N ₂	αCO ₂ /CH ₄	Reference
Pebax®1074/PEG1500	Pure gases		60		528		10.6	7,4	18
Pebax® MH1657/PEGDME500	Pure gases		30		650				18
Pebax® MH1657/PEG-AE	Pure gases		30		335				18
Pebax® MH1657/PEG-DVE	Pure gases		30		570				18
Pebax® MH1657/PEG-AME	Pure gases		30		620				18
Pebax®1657/PEGDME500	Pure gases		57		940		30		18
Pebax® 2533/PEG-b-PPFPA	Pure gases		35		940		17		18
EBA-zeolite4a	Pure gases			24.51	155.7		94.2	41.3	67, 69
PEBA/PEG/ZnO	Pure gases			7	94.49			31.59	67, 70
РЕВА	Pure gases	PSf	25			681	63		67, 71
PDMS/PEBA	Pure gases	PES/PE	57			940	30		19,67
PEBA-PS colloid	Pure gases		21	2.24	44		66		67, 72
РЕВА	Pure gases	PVC		10		3	55.5	25.8	67, 73
PEBA/PEG/NaX	Pure gases			8	95			45	67, 74

Table 26. High performance membranes for CO₂ separation

⁶⁹ Murali, Racha & Ismail, Ahmad & Rahman, Mukhlis & Sridhar, S. (2014). Mixed matrix membranes of Pebax-1657 loaded with 4A zeolite for gaseous separations. Separation and Purification Technology.

⁷⁰ Jazebizadeh, M.H., Khazraei, S. Investigation of Methane and Carbon Dioxide Gases Permeability Through PEBAX/PEG/ZnO Nanoparticle Mixed Matrix Membrane. Silicon 9, 775–784 (2017).

⁷¹ Panyuan Li, Zhi Wang, Wen Li, Yanni Liu, Jixiao Wang, and Shichang Wang, High-Performance Multilayer Composite Membranes with Mussel-Inspired Polydopamine as a Versatile Molecular Bridge for CO2 Separation, ACS Applied Materials & Interfaces 2015 7 (28), 15481-15493

⁷² Yu, Bing, Cong, Hailin, Li, Zejing, Tang, Jianguo, and Zhao, Xiu Song (2013). Pebax-1657 nanocomposite membranes incorporated with nanoparticles/colloids/carbon nanotubes for CO2/N-2 and CO2/H-2 separation. Journal of Applied Polymer Science 130 (4) 2867-2876.

⁷³ Khalilinejad, I., Sanaeepur, H., Kargari, A. (2015). 'Preparation of Poly(ether-6-block amide)/PVC Thin Film Composite Membrane for CO2 Separation: Effect of Top Layer Thickness and Operating Parameters', Journal of Membrane Science and Research, 1(3), pp. 124-129.

⁷⁴ Mahmoudi, A., Asghari, M., & Zargar, V. (2015). CO2/CH4 separation through a novel commercializable three-phase PEBA/PEG/NaX nanocomposite membrane. Journal of Industrial and Engineering Chemistry, 23, 238-242.

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PEBA-MWCNT	Pure gases			30		329.4	78.6		67, 75
РЕВА	Pure gases	PAN	25	4		13.5		18	67, 76
РЕВА	Pure gases	PSF				61	32		67, 77
РЕВА	Pure gases	PE		39.22		0.12		52.4	67, 78
PEBA-ZIF7	Pure gases		25	3.75	145		97	30	67, 79
PEI/PDMS/PEBA	Pure gases	Porous Substrate	25	7.1	102		73		67, 80
PEBA-ZIF8	Pure gases	PES		8	758			16.1	67, 81
PEBA-PEG-b-PPFPA	Pure gases	PAN	35	3.5	1860		25		67, 82
PEBA-Janus-Silver	Pure gases		25	2	150		72.5	26.3	67, 82
PEBA-zeolite13X	Pure gases	PE	25	14	194.12	48.53	56.5	56	67

⁷⁵ R. Surya Murali, S. Sridhar, T. Sankarshana, and Y. V. L. Ravikumar, Gas Permeation Behavior of Pebax-1657 Nanocomposite Membrane Incorporated with Multiwalled Carbon Nanotubes, Industrial & Engineering Chemistry Research ,2010, 49 (14), 6530-6538

⁷⁶ Esposito, Elisa & Clarizia, Gabriele & Bernardo, Paola & Jansen, Johannes & Petrusova, Zuzana & Izak, Pavel & Curcio, Stefano & De Cindio, Bruno & Tasselli, F. (2015). Pebax®/PAN hollow fiber membranes for CO2/CH4 separation. Chemical Engineering and Processing. 94. 53-61.

⁷⁷ Zhao, J., Wang, Z., Wang, J., & Wang, S. (2006). Influence of heat-treatment on CO2 separation performance of novel fixed carrier composite membranes prepared by interfacial polymerization. Journal of Membrane Science, 283, 346-356.

⁷⁸ Li S, Wang Z, Yu X, Wang J, Wang S. High-performance membranes with multi-permselectivity for CO2 separation. Adv Mater. 2012 Jun 26;24(24):3196-200.

⁷⁹ Ren, Xiaoling & Ren, Jizhong & Deng, Maicun. (2012). Polr(amide-6-b-ethylene oxide) membrane for sour gas separation. Separation and Purification Technology. 89. 1–8.

⁸⁰ Jomekian, Abolfazl & Behbahani, Reza & Mohammadi, Toraj & Kargari, Ali. (2016). CO2/CH4 separation by high performance co-casted ZIF-8/Pebax 1657/PES mixed matrix membrane. Journal of Natural Gas Science and Engineering. 31.

⁸¹ Scofield, Joel et al. (2015). Development of Novel Fluorinated Additives for High Performance CO2Separation Thin-film Composite Membranes. Journal of Membrane Science. 499. ⁸² Zhou T et al. (2015). Janus composite nanoparticle-incorporated mixed matrix membranes for CO2 separation. Journal of Membrane Science. 489.



4.7 Industrial requirements

Biogas upgrading units require mechanical and thermal stability to ensure a robust process. This also includes the restrictions applied over contamination. Typically, biomethane quality ranges between 88-92 vol% CH₄ for low quality grid and >96 vol% for high quality grid. Methane slip for those ranges is typically less than 0.5% providing low product loss. For low quality grid membrane selectivity of CO₂/CH₄ has a typical value of 40 while permeability is expected to be in a range of 50-100 GPU. On the other hand, high quality grid is expected to have selectivity higher than 50 and permeability higher than 3.5mol/ m²·s·Pa.

Regardless the output quality, the operation pressure range may vary between 1 to 45 bars depending on the grid pressure requirements. This also indicates the difference in the power consumption which is typically less than 0.25-0.43 kWh/Nm³ inlet.

Biogas upgrading specification	Value	Unit
P _{CO2}	50-100	GPU
CO ₂ /CH ₄ selectivity	>50	
CH ₄ slip	<0.5	%
Temperature	up to 55	°C
Design pressure	up to 20	bar

Table 27. Target specification for biogas upgrading membrane-based carbon capture



5 POST-COMBUSTION CAPTURE

5.1 General introduction on CO₂ emissions

 CO_2 is generated in large quantities and emitted in the gaseous effluents of industrial and power production sites, and in smaller and distributed amounts in building heating, transportation, etc. In all cases, since process feedstocks and fuels are almost all of fossil origin, the CO_2 emitted contributes to the anthropogenic carbon emission, causing an increase of the CO_2 concentration in the atmosphere and contributing to climatic changes. Main industrial sectors contributing to the (concentrated) CO_2 emissions are represented by power plants, and energy intensive industries, according to the breakdown reported in Table 28 (emissions from transportation sector are not included).

According to recent Intergovernmental Panel on Climate Change (IPCC) reports, the global mean concentration of CO_2 in the atmosphere is now close to 400 ppm; however, the most comprehensive research states that the safe level of CO_2 concentration is below 350 ppm^{83,84}. The global population is estimated to be around 9.2 billion by 2050, and dependency on the fossil fuel will increase in the absence of alternative renewable energy source. This will lead to higher CO_2 emission in the near future and is expected to reach up to 570 ppm_v level by 2100 which may increase the overall temperature by 1.9 °C⁸⁵. The presence of CO_2 currently contributes to ~60% of the total climatic changes contributing to the greenhouse effect⁸⁶. Accordingly, there is a pressing demand to reduce the CO_2 level using different techniques⁸⁵.

At present, there are three alternatives to minimize the CO_2 emission to the environment. The first one is to reduce the fuel consumption by adopting more energy-efficient techniques. The second is by embracing renewable sources of energy rather than conventional fossils fuels. The third alternative is to develop techniques which can sequestrate, capture, and separate CO2 easily and economically.

5.2 Market size

Even though CO₂ capture technologies are available in the market, the research showed that there is no incentive for the industrial parties to implement this type of technology. Carbon capture and storage may help to mitigate CO₂ emissions in the short term; however, it is costly, as approximately 10-40% of the energy of a given power plant is required to capture and store the carbon emissions it thereby produces by fossil fuel consumption (CO₂ concentration 8-10%)⁸⁷. As an indication, the price for CO₂ capture may range between 35 and 60 \notin per ton (CO₂ captured), while the EU allowances (EUA) for CO₂ costs are around 25 \notin /ton. However, as shown in Figure 23, there is a general expectation by analysts that the carbon price will likely keep increasing in the next years. The trend upwards is particularly significant in the short-to-mid-term, with ICIS forecasting EUA prices to top above \notin 40/tCO₂e by 2024. In the longer-term, we can notice

⁸³ F. A. Rahman et al., "Pollution to solution: Capture and sequestration of carbon dioxide (CO2) and its utilization as a renewable energy source for a sustainable future," Renew. Sustain. Energy Rev., vol. 71, no. January, pp. 112–126, 2017.

⁸⁴ R. Wennersten, Q. Sun, and H. Li, "The future potential for Carbon Capture and Storage in climate change mitigation - An overview from perspectives of technology, economy and risk," J. Clean. Prod., vol. 103, pp. 724–736, 2015.

⁸⁵ B. Prasad, R. Borgohain, and B. Mandal, "Advances in Bio-based Polymer Membranes for CO2 Separation.," in Advances in Sustainable Polymers, K. Vimal, A. Kumar, and N. Mulchandani, Eds. Singapore: Springer, Singapore, 2019, pp. 277–301.

⁸⁶ J. Oexmann, A. Kather, S. Linnenberg, and U. Liebenthal, "Review: Common attributes of hydraulically fractured oil and gas production and CO2 geological sequestration," Greenh. Gases Sci. Technol., vol. 2, no. 5, pp. 80–98, 2012.

⁸⁷ Source: De sleutelrol waarmaken Routekaart Chemie 2012-2030 Energie en klimaat, "https://traxxys.com/wp-content/uploads/2017/04/Routekaart-Chemie.pdf"



expectations to converge in 2028, between \notin 22 and \notin 27, while diverging again at the end of Phase 4, when the price range widens between \notin 15 and \notin 35.



Figure 23. EUA price forecasting⁸⁷

Concentrating a stream of 400 ppm CO_2 from delocalized emitters via direct air capture (DAC) will inherently be more expensive than capture at point sources. The low technology readiness level of many DAC technologies makes their cost estimates uncertain at this stage. What is clear is that DAC requires technological breakthroughs to become economically viable⁸⁷.

5.3 System providers

As the market still needs to develop in this area, membrane system provider for this applications could not be drafted.

5.4 Technology overview for post-combustion capture

There are many ways to capture large-scale quantities of carbon from various industries, such as coal-fired power and biomass plants, and there is an effort to develop potential CO_2 applications that could, at least in part, economically support the deployment of CCS technologies. Given the massive magnitude of the annual anthropogenic CO_2 emissions, a critical issue in the assessment of CO_2 capture and utilization technologies is to investigate the potential sources and also potential utilizing industries along with their scales. Table 28 provides a list of some anthropogenic CO_2 sources, sinks, and the scales. Unlike the sources, data on CO_2 utilization potentials is very scattered and is subject to a notable uncertainty. Currently, the total global CO_2 utilization is less than 200 million tonnes per annum (Table 28, last column) which is relatively negligible compared to the extent of global anthropogenic CO_2 emissions of more than 32,000 million tonnes per annum⁸⁸.

⁸⁸ A. Rafiee, K. Rajab Khalilpour, D. Milani, and M. Panahi, "Trends in CO2 conversion and utilization: A review from process systems perspective," J. Environ. Chem. Eng., vol. 6, no. 5, pp. 5771–5794, 2018.



CO2 emissions by economic		Large scale emiss	sion sources	Current CO2 uti	lization	
sector		(plants > 0.1 Mt _c	(v/v)			
Sector	Mtco2 (%)	Process	Number of sources	Emissions (Mtco2/v)	Industry	Usage (Mtco2/v)
Electricity and Heat Production	13,655.6 (42.4)	Power	4,942	10,539	Urea	114
Transportation	7,384.9 (23)	Cement Production	1,175	932	Methanol	8
Manufacturing Industries and Construction	6,144.8 (19.0)	Refineries	638	798	Dimethyl ether (DME)	3
Residential	1868.7 (5.8)	Iron and Steel industries	269	646	Methyl tert- butyl ether (TBME)	1.5
Services	861.9 (2.7)	Petrochemical industries	470	379	Formaldehyde (CH2O)	3.5
Other (agriculture/forestry,	2303,8 (7.2)	Oil and gas processing	NA	50	Carbonates	0.005
fishing, energy		Other sources	90	33	Polycarbonates	0.01
industries other than electricity and heat		Bioethanol and bioenergy	303	91	Inorganic Carbonates	50
generation, marine					Technological	28
bunkers)					Algae for production of biodiesel	0.01
Total	32189.7 (100)	Total	7,887	13,466	Total	200

Table 28.	Anthropogenic	sources, sinks	and	the scales ⁸⁸

However, the implementation of carbon dioxide capture and storage/utilization (CCS/CCU) technologies for most industrial activities – for example boilers, turbines, iron & steel furnaces and cement kilns requires a mandatory capture step to convert a relatively diluted stream of CO_2 to a higher concentration to allow economic transportation and storage. CO_2 capture technologies are available in the market but are costly in general and contribute to around 70–80% of the total cost of a full CCS system including capture, transport and storage system⁸⁹. Therefore, significant R&D efforts are focused on the reduction of operating costs and energy penalty⁹⁰. There are three main CO_2 capture systems associated with different combustion processes, namely, post-combustion, pre-combustion and oxyfuel combustion.

The present deliverable will focus only in post combustion processes, and in Figure 24 is shown the schematic of a post-combustion carbon capture process from an electricity generation plant. Post-combustion involves the treatment of the exhaust gases containing CO_2 on the product side with most of the CO_2 getting separated before releasing to the atmosphere.

⁸⁹ E. Blomen, C. Hendriks, and F. Neele, "Capture technologies: Improvements and promising developments," Energy Procedia, vol. 1, no. 1, pp. 1505–1512, 2009.

⁹⁰ D. Y. C. Leung, G. Caramanna, and M. M. Maroto-Valer, "An overview of current status of carbon dioxide capture and storage technologies," Renew. Sustain. Energy Rev., vol. 39, pp. 426–443, 2014.



Figure 24. Schematic representation of CO₂ capture in a post combustion application

In this method, the CO₂ has low partial pressure as it uses air for combustion which has high nitrogen content and hence low CO₂ (~15%) concentration⁸⁶. The energy requirement is little higher for the CO₂ capture in the post-combustion method, as excess dust and impurities (SO_x, NO_x, and incondensable gases) along with CO₂ are also produced, and therefore they need to be separated before CO₂ separation⁸⁵. However, the main advantage of post-combustion process is that it can be used in the existing industrial plants (e.g., power plant, steel production industries, cement, iron industries, etc.)⁸⁶.

Stream sources CO ₂ concentration - %vol		Pressure range	CO2 partial pressure
Gas turbines	3 - 4	Atmospheric	0.03 - 0.04
Fired boilers of Oil Refinery	8	Atmospheric	0.08
and Petrochemical plant			
Natural gas fired boiler	7 - 10	Atmospheric	0.07 - 0.1
Oil fired boilers	11 – 13	Atmospheric	0.11 - 0.13
Coal fired boilers	12 - 14	Atmospheric	0.12 - 0.14
IGCC after combustion	12 - 14	Atmospheric	0.12 - 0.14
Blast Furnace (after	27	Atmospheric	0.27
combustion)			
Cement Process	14 - 33	Atmospheric	0.14 - 0.33

Table 29. Typical conditions of a flue gas stream from various sources⁹¹

Further it can be fitted to the power plants and has the liberty to connect/disconnect or upgrade according to the requirements. Indeed, it is an end-of-pipe solution where CO₂ is removed from the flue emitted to the atmosphere via stack. Hence, post-combustion process has great suitability for CO₂ reduction from various fossil fuel burning industries. The main challenge is that the CO₂ level in combustion flue gases is usually quite low, about 7-14% for coal-fired and as low as 4% for gas fired⁹⁰. In Table 29 above, different flue gas qualities from various sources are illustrated. Carbon dioxide can be separated from the flue/fuel gas stream by several separation techniques, as discussed in the previous Chapters, such as, liquid phase absorption technologies, adsorption processes, membrane-based technology, cryogenic distillation, calcium looping technology⁹⁰. A qualitative description of each technology is outlined in the following sections.

⁹¹ and L. A. M. (eds.). Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, "IPCC, 2005: IPCC Special Report on Carbon Dioxide Capture and Storage," 2005.



5.4.1 Chemical absorption

The most mature and common form of post-combustion carbon capture is chemical absorption. For this application, the classic chemical absorbent for CO_2 separation applications is 20–30 wt% aqueous monoethanolamine (MEA). MEA is particularly suited to low CO_2 partial pressure applications and as a consequence has become the benchmark amine for CO_2 capture from electricity generation, and it is widely applied in the industrial landscape. In a standard CO_2 separation process applied to flue gas (10–15 kPa CO_2) at 40 °C, and using 30 wt% MEA and 90% CO_2 removal, typical minimum stripper reboiler duties are ~3.6–4.0 GJ per tonne CO_2 captured. The reboiler energy requirement is not the only metric that defines the performance of an absorbent, but reducing this value is the primary goal of much chemical absorbent research, and new absorbents are typically benchmarked against the value for 30 wt% MEA⁹². The difference between pre-combustion and post-combustion chemical absorption lies in the performance and the specific capture costs^{93,94}.

As it is illustrated in Figure 25, a typical absorption process consists of an absorber and a stripper column in which an aqueous solution of the selected chemical solvents is circulated acting as absorbent in the first stage and being regenerated in the second stage. The flue gas enters the absorber at the bottom and flows upwards while the solvent solution goes downwards, forming a counterflow. Through the contact of these two streams, part of the CO_2 in the flue gas is absorbed into amine solution. Then the solution with absorbed CO_2 , which is usually called rich-loaded solution, is pumped up to the head of the other column, the stripper. In the stripper, there is also a counter-flow occurring with rich-loaded solution flowing down the column and stripping stream generated in the reboiler upwards. With the heat from the stripping stream chemical bonds between CO_2 and solvent are broken so that CO_2 is carried up by the ascending steam towards the overhead condenser. Whilst the condensed steam is directed back to the stripper as a reflux, the product stream with high CO_2 purity (around 99%) is obtained. Then the product stream can be compressed for transportation to storage sites¹⁰. MEA the most energy intensive method since it entails the creation of a chemical bond between CO_2 and the solvent which needs to be broken during the sorbent regeneration step.

⁹² M. Bui et al., "Carbon capture and storage (CCS): the way forward," Energy Environ. Sci., vol. 11, no. 5, pp. 1062–1176, 2018.

⁹³ Y. Takamura, S. Narita, J. Aoki, and S. Uchida, "Application of high-pressure swing adsorption process for improvement of CO2 recovery system from flue gas," Can. J. Chem. Eng., 2001.

⁹⁴ "https://www.engineering-airliquide.com/rectisoltm-syngas-purification.".



Figure 25. Typical flowsheet of a basic chemical absorption process for CO₂ capture

R&D of new absorbents for flue gas applications has been ongoing for a number of decades. These new absorbents perform better than MEA in some or all of these characteristics. This suggests it may be time to move on from MEA and choose one of the new generation of absorbents for benchmarking purposes. Chemical absorbents can be divided in:

- Amine-based chemical absorbents
 - Single amine absorbents (BASF's activated MDEA, EDA, etc.);
 - Amine blends (e.g. blend of PZ and AMP)
- Multi-phase absorbents
 - *Liquid-solid* separation systems (in which Aqueous ammonia (NH₃) which is the most advanced of the multi-phase absorbent processes, Aqueous potassium carbonate (K₂CO₃), Amino acids);
 - *Liquid-liquid* phase separation systems (low critical solution temperature LCST, mutual solubility type and extraction type)¹⁰.

However, a range of new blends are progressing through bench scale testing and assessment including ternary blends.

On the other hand, physical absorption is less selective and can reach lower percentages of CO_2 recovery, but it has the advantage of a much lower energy consumption. It is applicable when the gaseous stream has a higher CO_2 vol%, which results in higher partial pressure (like in lean natural gas, biogas etc..), since physical absorption is controlled by Henry's law. One of the main advantages of this method is that CO_2 may be recovered mainly by depressurization, thereby avoiding the high heat consumption of amine scrubbing process. This method is widely applied for the removal of CO_2 from process syngas, such as in ammonia and methanol plants, since the high syngas pressure allows to obtain acceptable carbon dioxide partial pressures even with molar fractions around 20%. One of the most diffused technology based on



physical absorption utilizes a mixture of dimethyl ethers of polyethylene glycols (SelexolTM); the Rectisol® process is based on methanol and Fluor SolventTM utilizes propylene carbonate⁹⁴.

In general, the economics of CO_2 recovery is strongly influenced by the partial pressure of CO_2 in the feed gas. At low partial pressures, physical solvents are impractical because the compression of the gas for physical absorption is expensive. However, if the gas is available at high pressure, physical solvents might be a better choice than chemical solvents. This makes physical solvents particularly suitable for CO_2 removal from synthesis gas, and therefore applicable for pre-combustion capture, while their application in post-combustion capture is more energy intensive due to the low CO_2 partial pressure¹³.

5.4.2 Adsorption-absorption by solid materials

In contrast to absorption processes, which use a liquid absorbent, a solid sorbent is used to bind the CO_2 on its surface. Large specific surface area, high selectivity and high regeneration ability are the main criteria for sorbent selection. Typical sorbents include molecular sieves, activated carbon, zeolites, hydrotalcites.

In this process, CO_2 is preferentially adsorbed on the surface of a solid adsorbent at high pressure. Then the adsorbed CO_2 can be recovered by swinging the pressure (PSA) or temperature (TSA) of the system containing the CO_2 -saturated sorbent. PSA is a commercial available technology for CO_2 recovery from power plants that can have efficiency higher than 85 %^{90,93} In TSA, the adsorbed CO_2 will be released by increasing the system temperature using hot air or steam injection. The regeneration time is normally longer than PSA but CO_2 purity higher than 95% and recovery higher than 80% can be achieved^{90,95}. An operating cost of a specific TSA process was estimated to be of the order of 80–150 US \$/tonne CO₂ captured^{90,96}.

Finally, the use of residues from industrial and agricultural operations to develop sorbents for CO₂ capture has attracted significant attention to reduce the total costs of capture. Other solid sorbents, classified as high temperature sorbents, are also used in CO₂ capture processes based on solid materials. These processes are referred to solid looping cycles and rely on TSA principle. Some examples are the Calcium Looping and Sorption-Enhanced Reforming processes. They can be operated in either fluidized bed reactors with circulation of solids in a continuous mode, or in multi fixed bed reactors in a semi-continuous mode ^{97,98}.

5.4.2.1 Calcium Looping

Calcium looping (CaL) technology is a relatively new alternative for post-combustion CO_2 capture⁹², and is based on the following reversible reaction:

 $CaCO_3 \leftrightarrow 2CaO + CO_2$ $\Delta H = -178 \text{ kJ mol}^{-1}$

Implicit in such a cycle is the requirement that the lime product be used in multiple cycles in order to minimise the costs, and increase the overall efficiency of the process and this demands the use of a

⁹⁵ M. Clausse, J. Merel, and F. Meunier, "Numerical parametric study on CO2 capture by indirect thermal swing adsorption," Int. J. Greenh. Gas Control, 2011.

⁹⁶ A. R. Kulkarni and D. S. Sholl, "Analysis of equilibrium-based TSA processes for direct capture of CO 2 from Air," Ind. Eng. Chem. Res., 2012.

⁹⁷ S. S. Kazi, A. Aranda, J. Meyer, and J. Mastin, "High performance CaO-based sorbents for pre- And postcombustion CO2 capture at high temperature," 2014.

⁹⁸ S. Stendardo, L. K. Andersen, and C. Herce, "Self-activation and effect of regeneration conditions in CO2-carbonate looping with CaO-Ca12Al14O33 sorbent," Chem. Eng. J., 2013.



carbonator and a regenerator, normally envisaged as being a small oxy-fuel power plant to regenerate the spent sorbent and produce a pure stream of CO₂ for storage, or possibly use.

Calcium Looping technology is distinguishable from the other CCS technologies for three main reasons. First, because the carbonator/calciner can serve as a heat source for a steam cycle to produce additional power, the energy penalty associated with the technology can be several percentage points lower than that of conventional amine scrubbing. Second, the sorbent used, namely limestone, is available in industrial quantities, and is also a non-hazardous chemical whose price is of the order of US\$ 13–26 per tonne. In contrast, the cost of amine solvent MEA is much greater at US\$ 1.8–2.9 kg⁻¹. The third benefit of CaL is that there is a possibility of using the spent sorbent in industrial processes such as cement making, which, since lime manufacture represents 50% or more of the CO_2 output in cement production, offers an approach to partially decarbonise the cement industry or even to achieve near-zero emissions by incorporating the technology into the cement manufacturing process. CaL technology has also been progressed to pilot scale. There are two major demonstration projects, one at the University of Darmstadt, in Germany and one in La Pereda, Spain, which have been used to extensively test circulating fluidised bed-based technology, and a 1.9 MW_{th} pilot plant, which combines a bubbling fluidised bed carbonator and a rotary kiln calciner, in Taiwan that has been reported to have run for over 1 year. Based on its work, Industrial Technology Research Institute (ITRI) estimated that the integrated CaL process would offer a carbon capture cost of less than \$30 per tonne of CO₂. These demonstration projects mean that the technology has achieved a technical readiness level (TRL) of 6.

Moreover, there is now an extensive number of small pilot plant facilities worldwide being used to address various aspects of the technology, from looking at aspects of CaL, such as sorbent attrition, and the behaviour of modified and synthetic sorbents to improve their overall performance, to the development of novel configurations for CaL applications.



Figure 26. Schematic of the calcium looping (CaL) cycle⁹²



5.4.3 Cryogenic distillation

Cryogenic distillation is a gas separation process using distillation at very low temperature and high pressure, which is like other conventional distillation processes except that it is used to separate components of gaseous mixture (due to their different boiling points) instead of liquid. For CO₂ separation, flue gas containing CO₂ is cooled to its de-sublimation temperature (-100 to -135 °C) and then solidified CO₂ is separated from other light gases and compressed to a high pressure of 100–200 times the atmospheric pressure. The amount of CO₂ recovered can reach 90–95% of the flue gas⁹⁰. Since the distillation is conducted at extremely low temperature and high pressure, it is an energy intensive process estimated to be 600–660 kWh per tonne of CO₂ recovered in liquid form^{90,99}.

Cryogenic fractionation has the advantage that the CO₂ can be obtained at relatively high pressure as opposed to the other methods of recovering CO₂. This advantage may, however, be offset by the large refrigeration energy requirement. Special materials are also required for cryogenic service. This process is usually employed with the purpose of liquefaction and purification of CO₂ from high purity (>90%) sources. In cryogenic separation, there is separation of the CO₂ from the flue gas stream by condensation and vaporization cycles, separating the CO₂ from other gases such as CH₄ and N₂ based on their different vapor pressures and volatilities. This process involves the cooling of the gases to very low temperatures in order to liquefy and separate the CO₂. However, this process uses a high amount of energy to provide refrigeration and requires removing components that have freezing points above normal operating temperatures in order to avoid blockage of the equipment of the process. Also, for post-combustion flue gases, the by-products contained in the waste streams, such as NO_x and SO_x, must be removed before the introduction of the stream in the low temperature section, making it less economical than other post-combustion capture processes.

5.4.4 Membrane separation

Separation of CO_2 from flue gas streams is generally considered as a difficult application for any separation technology. The problems are the low CO_2 concentration and low pressure of the feed gas, coupled with huge gas flows. The enormous volumetric flowrate of a power plant flue gas stream means plants with very large membrane areas are required. However, producing membranes for this application is not the principal problem preventing adoption of post-combustion membrane systems for CO_2 treatment. Separating CO_2 from N_2 is an easy separation for membranes, and membranes with high permeances and high CO_2/N_2 selectivities have been developed. The more difficult problems to overcome are the scale of the process and the very large, expensive, and energy-consuming compression equipment needed¹⁰⁰. Indeed, in the post combustion application of membrane systems as end-of-pipe solution, flue gases to be treated are at atmospheric pressure conditions and carbon dioxide is diluted in nitrogen with a volume fraction typically between 4% (i.e. gas turbine) and 15% (coal combustion power plant); these two specificities address a major engineering challenge, especially in terms of the energy requirement of the separation process^{101,102}. Despite these difficulties to overcome, the membrane technology is proven as an alternative to high energy

⁹⁹ G. Göttlicher and R. Pruschek, "Comparison of CO2 removal systems for fossil-fuelled power plant processes," Energy Conversion and Management. 1997.

¹⁰⁰ T. C. Merkel, H. Lin, X. Wei, and R. Baker, "Power plant post-combustion carbon dioxide capture: An opportunity for membranes," J. Memb. Sci., 2010.

¹⁰¹ Steeneveldt R., Berger B., Torp T.A. (2006) CO2 capture and storage: closing the knowing doing gap, Chemical Engineering Research Development 84-A9, 739-763

¹⁰² Herzog H. (2001) What future for carbon capture and sequestration? Environmental Science Technology 35, 148A-153A.



consuming separation processes (thinking of reverse osmosis, air separation or ammonia production) and adapting it is attractive to industrial applications for many reason, such as simple operation and low maintenance cost as it does not have moving parts, has relatively low capital cost and small physical footprint¹⁰³.

Compared to other carbon capture processes, membrane separations show a high parametric sensitivity and the following variables will play a key role¹⁰⁴:

- feed conditions through the inlet CO_2 content (x_{in});
- driving force, expressed through the pressure ratio across the membrane (y = P''/P');
- material properties: the membrane selectivity ($\alpha = P_{CO_2}/P_{N_2}$) and CO₂ permeance.

Currently membrane technology is in pilot phase with respect to post-combustion capture.

5.5 System configurations

5.5.1 Process systems design for MPCC and module configurations

The objective of membrane system engineering (MSE) is to design the entire membrane process systems in optimal configurations to achieve required purities at minimum capital and operational expenditures (CAPEX and OPEX). Modelling and optimization are essential in MSE work. The concept of application of membranes for PCC is not fully explored and significant design optimization would be required in order to identify efficient, feasible, and environmentally sound technical solutions¹⁰⁵.

It is already found that single stage system cannot yield desired product with high CO_2 capture degree and purity. This is because the separation process is restricted on one hand by the low CO_2 partial pressure difference and on the other hand by the trade-off relationship between CO_2 capture degree and CO_2 purity¹⁰. Therefore, multi-stage or cascade membrane separation becomes a viable option. Two-stage separation system is more widely investigated.

5.5.2 Single-stage membrane process

Figure 27 illustrates a basic CO_2 capture process using membrane separation. Before entering the membrane module, a wet scrubber is often used to cool down the flue gas to the operational temperature of the membrane. Inside the membrane module, a portion of CO_2 permeate through the membrane and a stream (permeate gas) with higher CO_2 concentration is gained on the permeate side¹⁰.

¹⁰³ Ali Alshehri, Rajab Khalilpour, Ali Abbas, Zhiping Lai (2013) Membrane systems Engineering for Post-combustion Carbon Capture. Energy Procedia 37 (2013) 976 – 985

¹⁰⁴ Bouchra Belaissaoui, Eric Favre. Membrane Separation Processes for Post-Combustion Carbon Dioxide Capture: State of the Art and Critical Overview. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles, Institut Français du Pétrole, 2014, 69 (6), pp.1005-1020.

¹⁰⁵ R. Khalilpour, K. Mumford, H. Zhai, A. Abbas, G. Stevens, and E. S. Rubin, "Membrane-based carbon capture from flue gas: A review," J. Clean. Prod., vol. 103, pp. 286–300, 2015.



Figure 27. Schematic of a single step membrane-based separation process

The left part of the flue gas is called retentate gas. As mentioned above, the partial pressure of CO_2 is very small so that compressor and vacuum pump are used to increase the partial pressure difference between the feed and the permeate side. Similar to CO_2 capture degree in chemical absorption process, separation degree is used to indicate the proportion of CO_2 separated from flue gas. Compared to chemical absorption process, the membrane separation process apparently is simpler and contains less components. The major energy consumption comes from compressor and vacuum pump¹⁰.

5.5.3 Multi-stage membrane

In most of the flue gas cases, the concentration of CO₂ is notably low (Table 2). At such conditions, a single-stage membrane cannot produce high quality permeate or retentate even at very high inlet pressures and/or over large membrane areas. The solution is a combination of a few-stage membrane, in parallel or in series to reach higher qualities of permeate and retentate. Such arrangements result in higher CAPEX (due to high membrane area) and OPEX (due to high compression costs) making the appropriacy of membrane debatable for such conditions of low concentration feeds. In such scenarios, membranes may not be the best available technology (BAT) and other separation technologies might be competitive. Selection of the right option will therefore require detailed techno-economical investigations. The success of membrane systems will be very much dependent on process synthesis, configuration, and design¹⁰⁵.

Indeed, when the concentration of target component j in the feed gas (x_j) is low, even high-pressure ratios (b) may not achieve high permeate purity (y_j) . As such, more stages are required in order to achieve the desired quality and high recovery.



Figure 28. Schematic of cascade membrane system with recycle



However, it is well known that the most techno-economically optimal configuration is represented by the two- or three-stage membrane system, except in case of very low feed concentrations or low efficiency membrane.



Figure 29. Schematic of two-stage membrane system¹⁰⁵

Indeed, it has been shown that the introduction of more stages slightly decreases the membrane surface area and compression energy while subsequently increasing the number of compressors, thereby neutralizing that benefit¹⁰⁶. Figure 29 shows an example of two/three-stage membrane system for CO_2 separation. Bernardo et al.¹⁰⁷ in a thorough review of state of the art membranes for gas separation point out the fact that the concept of application of membranes for PCC is not fully explored and "significant design optimization would be required in order to identify efficient, feasible, and environmentally sound technical solutions"¹⁰⁵.

5.6 Membranes' materials for CO₂/N₂ separation

It is well known that membrane material plays a significant role in separating CO_2 from flue gas. Seader and Henley¹⁰⁸ have identified six attributes for a desirable membrane: (1) good permeability, (2) high selectivity, (3) chemical and mechanical compatibility with the process environment, (4) stability, freedom from fouling, and reasonable useful lifetime, (5) amenability to fabrication and packaging, and (6) resistance to high pressures. There is a limited number of commercial membranes that can be used for postcombustion CO_2 separation¹⁰⁹. Most of them have already been tested at coal-fired power plants. The results are summarized in Table 30.

Manufacturer	Membrane	Permeance [GPU]	CO ₂ /N ₂	Polymer
			Selectivity	
Air Liquide	Medal	Referred only	50	PI
		normalized		
Air Products	PRISM TM	760	13	PSf
MTR	Polaris™ gen1	1000	50	PE-PA copolymer
	Polaris [™] gen2	2000	49	PE-PA copolymer
Helmoltz-Zentrum	Polyactive TM	1480	55	PEO-PBT
PermSelect	PermSelect®	32.5	12	PDMS

Table 30. Commercially available tested membrane modules tested with flue gas¹⁰⁹

From the above it can be concluded that, although the commercial membrane modules have already been tested on some level in the real conditions, there are still many issues to be solved especially those connected

¹⁰⁶ S. Liguori and J. Wilcox, "Design considerations for postcombustion CO2 capture with membranes," Curr. Trends Futur. Dev. Membr. Carbon Dioxide Sep. by Using Membr., pp. 385–413, 2018.

¹⁰⁷ P. Bernardo, E. Drioli, and G. Golemme, "Ind. Eng. Chem. Res. 2009, 48, 4638–4663 Gas Sep State of the art Bernardo et al.pdf," pp. 4638–4663, 2009.

¹⁰⁸ J. D. Seader, W. D. Seider, D. R. Lewin, L. Boulle, and A. Rycrof, Separation Process Principles, 3rd Edition. 2006.

¹⁰⁹ M. Kárászová et al., "Post-combustion carbon capture by membrane separation, Review," Sep. Purif. Technol., vol. 238, no. August 2019, 2020.



with the durability of the membrane materials. That is why a great effort is still put into the development of new membrane materials.

Twenty-seven membrane materials of different kinds are presented in Table 31. The data are published since 2013 and declared by their authors as convenient for flue gas separation. Four of these materials were tested at the pilot scale in power plants and the results show what should be solved in the near future for wider applicability in the flue gas treatment. The basic research has focused on various membrane materials in recent years. CO_2 separation is studied in two main configurations of membranes – flat sheet and hollow fiber. A recently tested material is ceramic porous membranes. They are able to capture up to 90% of CO_2 from flue gas. Polymeric membranes also show very good permeability and selectivity. However, they suffer from the plasticization when CO_2 is separated from flue gas. Contrary, MMMs and metallic-organic frameworks (MOFs) seems to be promising membrane material combining the transport and separation properties of polymeric matrix with the stabilization by nanoparticle/metallic fillers. For CO_2 capture from flue gas, CO_2 -selective polymer membranes, PIM-based membranes, and thermal rearrangement (TR) membranes. Again, some of these membranes and their performance for CO_2/N_2 separation are listed in Table 30 above.



Table 31. Experimental membrane materials¹⁰⁹

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Membrane Type	Membrane	Permeability [Barrer]*	CO ₂ /N ₂ Selectivity	Note
SILM	[ATMPS][Ac] in polyimide 84	24*	40	
SILM	[Emim][Tf2N] and (Al(i-C3H7O)3) + SAPO 34 in PSf	7.24*	20.3	
LM in composite	Pebax®1657/[emim][BF4] gel membrane	280	42	
LM in MMM	GO-IL in Pebax 1657	143	71	
LM in MMM	polyionic liquid with free ionic liquid content on epoxide amine with facilitated carrier transport	900	140	
MMM	CA functionalized by Tf2N anion	8.9*	26.8	Did not enhance the CA properties
MMM	Pebax® membrane with pseudopeptide biconjugate additives	194	44	
МММ	Amino-functionalized polyhedral oligomeric silsesquioxane (amine-POSS®) nanoparticles dispersed in (PVA)	22.2*		Humidity effect: increase of CO ₂ permeance
MMM	Pebax/PTMEG	350	60	Depends on PTMEG content
MMM	PU with NiO nanoparticles	350	68	Depending on nanoparticle content
МММ	Contained Fe(BTC), benzene 1,3,5 tricarboxylate and iron octahedral clusters, with removable terminal ligands of H2O and OH incorporated in Matrimid	218	23	
MOF	NH2-MIL-53(Al) in CA	15.5	25	
MOF	PU/UiO-66 (Zr)	75*	34	T _{amb} and 4 bar
MOF	PU/MIL-101 (Cr)	83	42	T _{amb} and 4 bar
MOF	ZIF/300/Pebax 1657	102.1	73.9	298 K, 12 bar dry feed CO ₂ :N ₂ 15:85 (v/v)
MOF	ZIF/300/Pebax 1657	466.2	59.2	298 K, 12 bar CO ₂ :N ₂ 15:85 (v/v) feed relative humidity 85%
MOF	PEDM/ZIF-8@GO-6-6	475	58.2	Tests at 25°C under 1 bar
PIM	PIM-1	7500	19	
PIM in MMM	PIM-1 - Schiff base network	7600	22.4	
MMM in composite	Pebax/Zeolite Y composite membrane, with three layers on top of a polyethersulfone	795*	35	
Composite	Pebax without zeolite composite membrane, with three layers on top of a polyethersulfone	1420*	10	
Composite	Biomax PES with zeolite Y nanoparticles and Pebax/PEG 200 polymer selective layer	745*	25	
Composite	PEI (PVC-g-POEM)	35*		

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Hollow Fiber	Asymetric PES hollow fibers	50*	45	Selectivity from numer. model
TRP	Polybenzoxazol	-	-	
Fixed Carriers	Polyvinylamine as a fixed carries	222.2*	300	
Polymeric (modified PI)	Semi-alicyclic aromatic polyimide	8.6	28	
Ceramic	Ce _{0.8} Sm _{0.2} O _{1.9} (SDC)/Li ₂ CO ₃ -Na ₂ CO ₃ ceramic carbonate dual-phase membrane	-	192	SO ₂ poisoned CO ₂ permeation, temp 550– 750 °C
Ceramic	Amino-modified mesoporous ceramic membranes	30	22	

* For the thickness of membrane of $1 \mu m$, calculated from permeance.

Table 32. Membrane performance for CO₂/N₂ separation⁶

Membrane	Selective Layer	Feed Gas	Operation Conditions	CO ₂ Permeance (GPU)	CO ₂ /N ₂ Selectivity	References
Polvactive	<0.1	15/85 CO ₂ /N ₂	0.5-2 MPa, 20 °C	~1000	~55	Yave et al. (2010a)
Polyactive + PEG-DBE	~0.15	28/72 CO ₂ /N ₂	0.5 MPa, 20 °C	~800	40	Yave et al. (2010b)
PBT-PEO	~0.05	Pure Gas	30 °C	1300-1800	>50	Yave et al. (2011)
PEO-b-PES	-	Pure Gas	0.007 MPa, 70 °C	20, 400	27.7	Xue et al (2012)
PDMS	-	15/85 CO ₂ /N ₂	0.2 MPa, 25 °C	3700	10	Li et al. (2013b)
Pebax	<5	-	0.69 MPa, 25 °C	61	~32	Liu et al. (2004)
Pebax 1657/PEG	<2	25/75 CO ₂ /N ₂	0.7 MPa, 25 °C	84	63-70	Car et al. (2008)
PEG-PDMS BCP + Pebax	<1	Single Gas	0.35 MPa, 25 °C	~1000	21	Scofield et al. (2015)
Pebax-2533/PEG-b-PPFPA3	~0.52	Single Gas	0.35 MPa, 25 °C	1650	25	Scofield et al. (2016)
(40/60)						
Cross-linked PEG	~0.1	30/70 CO ₂ /N ₂	0.1 MPa, 25 °C	1210	~22	Fu et al. (2016)
DNMDAm-DGBAmE-TMC	~0.15	15/85 CO ₂ /N ₂	0.11 MPa, 25 °C	1600	138	Li et al. (2012a)
РАМАМ	~0.1	5/95 CO ₂ /N ₂	0.097 MPa, 40 °C	61	230	Duan et al. (2006)
PVAm-PIP	0.13-0.22	20/80 CO ₂ /N ₂	0.11 MPa, 25 °C	1700-6500	200-277	Qiao et al. (2013)
PVAm-PVA	~0.5	10/90 CO ₂ /N ₂	0.2 MPa, 25 °C	157	~150	Deng et al. (2009)
PVAm	0.7-1.5	10/90 CO ₂ /N ₂	0.1 MPa, 25 °C	453.22	68	Sandru et al. (2010)
PDMS-PDA-PVAm	0.5-1	15/85 CO ₂ /N ₂	0.11 MPa, 25 °C	1887	83.1	Li et al. (2015c)
Poly(N-vinylimidazole)-zinc	~0.12	15/85 CO ₂ /N ₂	0.11 MPa, 25 °C	1150	95.8	Yao et al. (2012)
complex DECDEM DOEM	1522	0: 1 0		1.2.117	01.04.7	D.1.(2015)
PEGBEM-g-POEM	1.5-2.3	Single Gas	КІ	1.3-117	2.1-84.7	Park et al. (2015)
PDMAEMA-PEGMEA	2	Single Gas	0.1 MPa, 25 °C	25	31	Ji et al. (2010)

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Cross-linked PVA-PVP	40-70	20/80 CO ₂ /N ₂	0.1 MPa, 25 °C	29	270	Mondal and Mandal (2014)
PIM-Trip-TB (aged 470 days)	132	Pure Gas	0.1 MPa, 25 °C	3951	20.9	Carta et al. (2014)
PIM-1/CNT	~0.65-0.77	-	-	10.548	34.4	Koshine et al. (2015)
PIM-300-2 d	~55	Pure Gas	0.1 MPa, 25 °C	4000	41.7	Li et al. (2012b)
TR-PBO500	~2	Pure Gas	0.1 MPa, 25 °C	2326	20	Kim et al. (2012)
PEEKWC	-	Pure Gas	0.1 MPa, 25 °C	3.1	33	Jansen et al. (2005)
PC	-	Pure Gas	0.2 MPa, 24±0.5 °C	10	25.1±0.8	Idris et al. (2017)
САВ	-	Pure Gas	0.2 MPa, 25 °C	120.19	3.17	Lee et al. (2017)
PEG-PES	-	Pure Gas	0.2 MPa, 25 °C	30	50	Chen et al. (2011)
PEI	-	Pure Gas	0.1 MPa, 25 °C	6.35	10.7	Ahmad et al. (2017)



5.6.1 CO₂-philic polymeric membrane materials

Similar to CO₂-selective membranes for CO₂ capture from syngas, introducing CO₂-philic functional groups is an effective strategy to enhance CO₂ solubility selectivity. Many block copolymers including rubbery segment with polar ether linkage and glassy segment have been extensively investigated. The research studies show that the hard segments can reduce the crystallization of polyether segments and improve the mechanical strength property. Some commercial PEO-based copolymers and membranes, such as Pebax, Polyactive, and Polaris, have shown moderate to high CO₂/N₂ separation performance as promising membrane materials for large-scale development. MTR, Inc. built a pilot membrane system (membrane Polaris, CO₂ permeance >1500 GPU) and tested at an NGCC power plant with a target of 20 ton/day CO₂ capture capacity. For CO₂-philic polymeric membrane materials, the not high enough selectivity may be the biggest limitation for post-combustion CO₂ capture⁶.

5.6.2 Polymers of intrinsic microporosity-based membrane materials

Enhancing solubility selectivity and diffusivity selectivity may be the most effective strategy to design novel high-performance PIM-based membranes for CO_2/N_2 separation. Moreover, improving the chain rigidity can improve CO_2 permeability of PIM membranes. Despite high thermal and chemical stabilities for PIMs materials, physical aging still limited the applications of PIM-based membranes, which could be even faster in the membrane with thinner selective layer⁶.

5.6.3 Thermal rearrangement membrane materials

TR polymers with high free volume and narrow cavity size distribution are promising membrane materials for post-combustion CO_2 separation applications, considering the superior tolerance to high temperature and chemical contaminants combined with their excellent separation performance. TR-PBO hollow fiber membranes with CO_2 permeance of around 2000 GPU could meet the required membrane performance for post-combustion CO_2 separation. However, competitive sorption and pore blockage resulted by the water in real flue gas may reduce the CO_2 permeance⁶.

5.7 Opportunities and challenges for CO₂/N₂ separation

 CO_2 capture from power plants and industrial exhaust gases can be significant for reducing man-made CO_2 emissions. Because post-combustion flue gas released from power generators at atmospheric pressure typically contain 4-20% CO_2 , high CO_2 permeance plays an important role in reducing the capital cost and energy consumption for CO_2 capture. The key is to find polymers with good CO_2/N_2 selectivity and the highest possible CO_2 permeability.

Rubbers containing PEO have shown moderate to high CO_2/N_2 separation performance as promising membrane materials for large-scale development. Today's best membranes made from PEO-based polymers have a CO_2 permeance of about 2000 GPU and a CO_2/N_2 selectivity of about 50. Another approach for better membranes is to incorporate CO_2 -reactive groups within the polymer matrix to produce a facilitated transport effect. Facilitated transport membrane materials show much higher CO_2/N_2 selectivities than the best polymeric materials. Moreover, increasing the CO_2 permeance is the key issue for facilitated transport membranes. Reducing the selective layer thickness can increase the permeances while improving the stability of thin membranes. The main drawback for facilitated transport membranes is that at a high CO_2 partial pressure, the carriers will be saturated by CO_2 and lose the facilitated transport effect. However, the low CO_2 concentration and the low feed gas pressure for CO_2 capture from flue gas



make facilitated transport membranes excellent candidates. Moreover, before industrial application, more long-term stability studies tested by real flue gas are needed for better evaluation. Despite high permeability, most PIMs materials are subject to significant physical aging. The dimensional stability of PIMs is a major issue because their rigidity does not alleviate plasticization in the presence of CO_2 . Scholes et al. investigated water vapor effects on gas separation properties of PIM-1. Water vapor only affects CO_2 and N₂ permeability to a similar extent with the nearly invariably CO_2/N_2 selectivity. Interestingly, PIMs exhibit greater selectivities under CO_2/N_2 mixed gas permeation experiments than CO_2/N_2 pure gas selectivities⁶.

Thermally rearranged polymers based on polybenzoxazoles (PBOs) are also attracting interest for CO_2/N_2 separation. However, the low solubility in most organic solvents for PBOs and physical aging are the main limits to applications for CO_2/N_2 separation. Wang et al. exploited gas permeability measurements to track physical aging of thick and thin films of TR polymers. As expected, thin (1-2 mm) films age more rapidly than thick films (20 mm), so thick films become more permeable than thin films over longer times. For CO_2 capture from flue gas, it is generally acknowledged that increasing CO_2 permeance for reducing membrane area and cost reduction is significantly more important in a second membrane stage and increasing selectivity beyond 40-50 will not be useful because of the practical limited pressure ratios. However, very high selectivities might be useful to obtain high-purity CO_2 products. The high performance PEO-based materials and facilitated transport membrane materials with relatively high tolerance to impurities and excellent film-forming properties are promising for CO_2/N_2 separation applications. Some PIM and TR polymers have also been reported with distinctive properties, but CO_2 permeance decline over time. Moreover, competitive sorption of impurities and plasticization can lower the performance. Finally, some aging does occur in glassy polymer membranes, and it could be even faster in thin films⁶.

5.8 Industrial requirements

An industrially desirable membrane requires (generally and specifically for carbon capture) other key features such as chemical and mechanical compatibility with the process environment, stability, freedom from fouling, reasonable useful lifetime, amenability to fabrication and packaging, and resistance to high pressures. Nevertheless, most of the existing studies on CO₂ capture membrane materials are focused on improving perm-selectivity and they lack sufficient attention to other important requirements. The impacts of minor gas components such as water vapor, O₂, SO_x, NO_x, NH₃, etc. have been widely ignored in the literature, with few exceptions, mainly focus on a binary mixture of N₂ and CO₂. As such, commercialization of membranes might not be possible without addressing these critical technical and operational concerns.

To be competitive with amine-based nth-of-a-kind (NOAK) technology or meet a more ambitious cost target for 90% CO₂ capture, advanced membranes should have a higher CO₂ permeance than 2,250 GPU and a higher CO₂/N₂ selectivity than 30 if their installed prices are higher than $50/m^{2110}$. For the prototypes to be fabricated, BIOCOMEM set the target of permeance P_{CO2} > 100 GPU and selectivity CO₂/N₂ > 70 respectively. Moreover, membranes should be stable up to 100 °C at 7 bar. Finally, the cost of these membranes will need to be < 100 €/m² for post-combustion. All these factors are summarized in Table 33.

¹¹⁰ Zhai, Haibo. (2019). Advanced Membranes and Learning Scale Required for Cost-Effective Post-Combustion Carbon Capture.
Table 33. Industrial requirements and targets for post-combustion membrane-based carbon capture

Post- combustion Specification	Value	Unit
Рсо2	2,250	GPU
CO ₂ /N ₂ selectivity	30	
Temperature	100	°C
Design pressure	7	bar
Costs	<100	€/m ²



6 ANNEXES

6.1 Annex 1

Hyperlinks Systems Suppliers

Air Liquide >> MEDAL and PoroGen PEEK-sep>> https://www.airliquideadvancedseparations.com/sites/medal/files/2016/11/28/alas ng brochure final.pdf

EVONIK >> SEPURAN NG >> <u>https://www.membrane-separation.com/en/natural-gas-processing-with-</u> sepuran-ng

UOP-Honeywell >> Separex >> <u>https://www.honeywell-uop.cn/wp-content/uploads/2015/11/uop-separex-membrane-systems-brochure1.pdf</u>

 $Schlumberger >> CYNARA >> \underline{https://www.slb.com/well-production/processing-and-separation/gastreatment/cynara-acid-gas-removal-membrane-systems}$

UBE >> Separation Membrane >>

http://www.ube.co.th/picture/file/CO2%20Separation%20Membrane.pdf#:~:text=UBE%27s%20polyimid e%20membrane%20is%20made%20of%20aromatic%20polyimide,membrane%20can%20be%20operate d%20up%20to%20100%20%C2%B0C

 $\label{eq:proSep} ProSep >> Natural gas Membranes >> <u>http://prosep.com/wp-content/uploads/2014/03/Gas-Membranes-Technology-Sheet-Letter.pdf</u>$

6.2 Annex 2

Wobbe index is an indicator of the interchangeability of fuel gases such as natural gas, liquefied petroleum gas (LPG), and town gas, It is frequently defined in the specifications of gas supply and transport utilities. The Wobbe Index is used to compare the combustion energy output of different composition of fuel gases in appliance. If two fuels have identical Wobbe Indices, then for a given pressure and valve settings, the energy output will also be identical. Typically variations of up to 5% are allowed as these would not be noticeable to the consumers¹¹¹.

¹¹¹ Nattadon Pannucharoenwong, Atichit Worasaen, Chatchai Benjapiyaporn, Jarinee Jongpluempiti, Ponthep Vengsungnle, Comparison of Bio-Methane Gas Wobbe Index In Different Animal Manure Substrate, Energy Procedia, Volume 138, 2017