



HAL
open science

Membrane Separation Processes for Post-Combustion Carbon Dioxide Capture: State of the Art and Critical Overview

Bouchra Belaïssaoui, Eric Favre

► **To cite this version:**

Bouchra Belaïssaoui, 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, 2014, 69 (6), pp.1005-1020. 10.2516/ogst/2013163 . hal-01274045

HAL Id: hal-01274045

<https://hal.univ-lorraine.fr/hal-01274045>

Submitted on 8 Dec 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



This paper is a part of the hereunder thematic dossier published in OGST Journal, Vol. 69, No. 6, pp. 977-1129 and available online [here](#)

Cet article fait partie du dossier thématique ci-dessous publié dans la revue OGST, Vol. 69, n°6, pp. 977-1129 et téléchargeable [ici](#)

DOSSIER Edited by/Sous la direction de : **P.-L. Carrette**

PART 2

Post Combustion CO₂ Capture Captage de CO₂ en postcombustion

Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 69 (2014), No. 6, pp. 977-1129

Copyright © 2014, IFP Energies nouvelles

- 977 > Editorial
- 989 > *Post-Combustion CO₂ Capture by Vacuum Swing Adsorption Using Zeolites – a Feasibility Study*
Captage du CO₂ en postcombustion par adsorption modulée en pression avec désorption sous vide sur zéolithes — étude de faisabilité
G. D. Pirngruber, V. Carlier and D. Leinekugel-le-Cocq
- 1005 > *Membrane Separation Processes for Post-Combustion Carbon Dioxide Capture: State of the Art and Critical Overview*
Procédés membranaires pour le captage du dioxyde de carbone : état de l'art et revue critique
B. Belaisaoui and É. Favre
- 1021 > *Pressure Drop, Capacity and Mass Transfer Area Requirements for Post-Combustion Carbon Capture by Solvents*
Pertes de charge, capacité et aires de transfert de matière requises pour le captage du CO₂ en postcombustion par solvants
A. Lassauce, P. Alix, L. Raynal, A. Royon-Lebeaud and Y. Haroun
- 1035 > *Hollow Fiber Membrane Contactors for Post-Combustion CO₂ Capture: A Scale-Up Study from Laboratory to Pilot Plant*
Captage postcombustion du CO₂ par des contacteurs membranaires de fibres creuses : de l'échelle laboratoire à l'échelle pilote industriel
É. Chabanon, E. Kimball, É. Favre, O. Lorain, E. Goetheer, D. Ferre, A. Gomez and P. Broutin
- 1047 > *Hollow Fiber Membrane Contactors for CO₂ Capture: Modeling and Up-Scaling to CO₂ Capture for an 800 MW_e Coal Power Station*
Contacteurs à membrane à fibres creuses pour la capture de CO₂ : modélisation et mise à l'échelle de la capture du CO₂ d'une centrale électrique au charbon de 800 MW_e
E. Kimball, A. Al-Azki, A. Gomez, E. Goetheer, N. Booth, D. Adams and D. Ferre
- 1059 > *Regeneration of Alkanolamine Solutions in Membrane Contactor Based on Novel Polynorbornene*
Régénération de solutions d'alcanolamine dans un contacteur à membrane basé sur un nouveau polynorbornène
A.A. Shutova, A.N. Trusov, M.V. Bermeshev, S.A. Legkov, M.L. Gringolts, E.Sh. Finkelstein, G.N. Bondarenko and A.V. Volkov
- 1069 > *Development of HiCapt+™ Process for CO₂ Capture from Lab to Industrial Pilot Plant*
Développement du procédé HiCapt+™ pour le captage du CO₂ : du laboratoire au pilote industriel
É. Lemaire, P. A. Bouillon and K. Lettat
- 1081 > *A Technical and Economical Evaluation of CO₂ Capture from Fluidized Catalytic Cracking (FCC) Flue Gas*
Évaluation technico-économique du captage du CO₂ présent dans les fumées d'une unité FCC (*Fluidized Catalytic Cracking*)
R. Digne, F. Feugnet and A. Gomez
- 1091 > *Pilot Plant Studies for CO₂ Capture from Waste Incinerator Flue Gas Using MEA Based Solvent*
Étude du captage du CO₂ dans des gaz de combustion d'un incinérateur de déchets à l'aide d'un pilote utilisant un solvant à base de MEA
I. Aouini, A. Ledoux, L. Estel and S. Mary
- 1105 > *Amine Solvent Regeneration for CO₂ Capture Using Geothermal Energy with Advanced Stripper Configurations*
Régénération d'un solvant de captage du CO₂ utilisant l'énergie géothermique et des configurations améliorées pour le régénérateur
D.H. Van Wagener, A. Gupta, G.T. Rochelle and S.L. Bryant
- 1121 > *ACACIA Project – Development of a Post-Combustion CO₂ capture process. Case of the DMX™ process*
Projet ACACIA – Développement d'un procédé de captage du CO₂ postcombustion – Cas du procédé DMX™
A. Gomez, P. Briot, L. Raynal, P. Broutin, M. Gimenez, M. Soazic, P. Cessat and S. Saisset

Membrane Separation Processes for Post-Combustion Carbon Dioxide Capture: State of the Art and Critical Overview

Bouchra Belaïssaoui and Eric Favre*

LRGP (UPR CNRS 3349), Université de Lorraine, 1 rue Grandville, 54001 Nancy - France
e-mail: bouchra.belaïssaoui@univ-lorraine.fr - eric.favre@univ-lorraine.fr

* Corresponding author

Résumé — Procédés membranaires pour le captage du dioxyde de carbone : état de l'art et revue critique — Les procédés de séparation par membrane ont été, dans un premier temps, rarement préconisés pour le captage du dioxyde de carbone en post-combustion, les procédés d'absorption gaz-liquide dans un solvant chimique étant considérés comme la technologie la plus mature et la plus adaptée pour assurer cette opération. Une revue critique des possibilités et limites des membranes pour le captage du CO₂ par perméation gazeuse est présentée. Les performances de différents types de matériaux membranaires (polymères denses, matériaux inorganiques, matrices hybrides, membranes liquides) sont discutées sur le plan de la sélectivité et de la perméabilité, en prenant en compte les résultats expérimentaux les plus récents dans ce domaine. Les caractéristiques d'une unité de perméation gazeuse mono-étagée fonctionnant en régime permanent, déterminées par simulation, sont ensuite détaillées, en particulier par rapport aux contraintes de pureté et de dépense énergétique de l'opération, en lien avec les performances du matériau. Finalement, les possibilités des dispositifs membranaires multi-étagés et des procédés hybrides associant une unité de perméation gazeuse et un autre procédé, encore peu étudiés dans la littérature sont évoquées, ainsi que les besoins d'analyse technico-économiques afin de mieux identifier la place et le rôle optimal des membranes pour le captage du CO₂.

Abstract — Membrane Separation Processes for Post-Combustion Carbon Dioxide Capture: State of the Art and Critical Overview — Membrane processes have been initially seldom considered within a post-combustion carbon dioxide capture framework. More traditional processes, particularly gas-liquid absorption in chemical solvents, are often considered as the most appropriate solution for the first generation of technologies. In this paper, a critical state of the art of gas separation membranes for CO₂ capture is proposed. In a first step, the key performances (selectivity, permeability) of different membrane materials such as polymers, inorganic membranes, hybrid matrices and liquid membranes, including recently reported results, are reviewed. In a second step, the process design characteristics of a single stage membrane unit are studied. Purity and energy constraints are analysed as a function of operating conditions and membrane materials performances. The interest of multistage and hybrid systems, two domains which have not sufficiently investigated up to now, are finally discussed. The importance of technico-economical analyses is highlighted in order to better estimate the optimal role of membranes for CCS applications.

NOMENCLATURE

E	Energy requirement ($\text{J}\cdot\text{ton}^{-1}$)
p'	Membrane module upstream side pressure (bar)
p''	Membrane module downstream side pressure (bar)
p	Pressure (bar)
P	Permeability coefficient (Barrer or $\text{mol}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ [SI])
Q	Flow rate ($\text{mol}\cdot\text{s}^{-1}$)
R	Recovery ratio (-)
R	Perfect gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
T	Temperature (K)
x_{in}	Mole fraction in the feed mixture (-)
y	Mole fraction in the permeate side (-)

GREEK LETTERS

α^*	Ideal separation factor (-)
γ	Adiabatic gas expansion coefficient (-)
ψ	Pressure ratio (-)
θ	Stage cut (-)
η_C	Compressor isentropic efficiency (-)
η_V	Vacuum pump efficiency (-)
η_E	Expander efficiency (-)

INTRODUCTION

The design of an efficient, low energy intensive and low cost CO_2 capture unit is of utmost importance for the deployment of Carbon Capture and Storage (CCS) technologies at industrial scale (Davidson and Metz, 2005). This statement particularly holds for the post-combustion framework. In that case, flue gases to be treated are under 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 (Steenveeldt *et al.*, 2006; Herzog, 2001).

Numerous capture technologies are being developed and evaluated for this application such as absorption in liquids, adsorption on solids, cryogenic processes, membranes, solid sorbents (Figueroa *et al.*, 2008). The overall framework is complex and the identification of the most efficient process is subject to controversial debates. Generally speaking, the ideal

carbon capture process should offer the following characteristics:

- a high CO_2 over N_2 selectivity, in order to achieve a concentration up to 90 to 99% CO_2 (before the compression, transport and storage steps);
- a minimal energy requirement, ideally below 2 GJ per ton of CO_2 (thermal basis), so that secondary CO_2 emissions generated by the capture process remain limited;
- a maximal productivity (sometimes also named capacity), which is required in order to minimize the size (footprint) of the capture unit;
- a minimal, if not negligible impact on environment, which can be assessed through criteria such as the waste produced by the capture unit (solids, liquid or gaseous emissions) and water footprint;
- a minimal overall cost of the unit, usually expressed in \$ (or €) per ton of CO_2 captured and including the operating (OPEX) plus capital (CAPEX) expenses.

Taking into account the different items listed above, gas liquid absorption in a chemical solvent (such as an aqueous amine solution) is currently considered as the best available and mature technology (Steenveeldt *et al.*, 2006). Amine solvents are used for decades for natural gas treatment. Amines effectively offer a very high selectivity towards CO_2 through carbamate formation; as a consequence a high purity CO_2 stream can be attained after drying the mixture generated in the stripping unit. The energy requirement essentially corresponds to the stripper boiling duty; this is achieved by low pressure steam (typically 2 bar), a largely available energy source in a power plant. The two major drawbacks of the amine absorption process correspond to a too high energy requirement (Steenveeldt *et al.*, 2006) (typically 3 GJ/ton in thermal basis, excluding compression) and the production of wastes: solids (heat stable salts) and traces of gaseous compounds due to amine degradation. New solvents or alternative separation processes which would not show these disadvantages are intensively explored for the second generation of carbon capture technologies.

Compared to other capture processes, membrane separation shows a very high parametric sensitivity, especially in terms of CO_2 content in the feed stream (Belaissaoui *et al.*, 2012a). Additionally, it has been shown that strong limitations occur when 90% capture ratio and 90% CO_2 purity are both imposed for a single stage process. More specifically, given the performance of existing membrane materials, the target purity and capture ratio of 90% can be attained in a single stage membrane module only providing that a flue gas stream with relatively concentrated CO_2 (typically above

20% CO₂) is to be treated (Favre, 2007). Besides, a very large majority of CO₂ sources has a lower CO₂ content, such as 15% for coal power plants or 5% for natural gas turbine flue gases. In these cases, multistage membrane units or hybrid process design are needed, unless a concerted effort is first made to increase the CO₂ concentration through a mixture of Flue Gas Recirculation (FGR), supplementary firing, and combustion using Oxygen Enhanced Air (OEA) (Belaisaoui *et al.*, 2012b).

Multistage membrane units and hybrid process design are discussed in more details in Section 4.

Generally speaking, membrane separation processes have been initially discarded for carbon capture (Davidson and Metz, 2005; Figueroa *et al.*, 2008). Arguments such as a too high energy requirement, the impossibility to develop highly selective materials, too expensive capital costs characteristics (*i.e.* no economy of scale due to a scale up strategy based on numbering up) have been alternatively proposed in order to justify their inadequacy (Favre, 2007). Nevertheless, the situation evolved these last years with numerous membrane material developments, which suggest the potentialities of membrane processes to be reconsidered. A limited number of process design studies has been however reported (Favre, 2007). It is worth to note that promising results have been recently reported on a pilot demonstration unit based on tailor made membrane modules, which has been launched in 2010 for the treatment of real flue gases in a coal power plant (Merkel *et al.*, 2010).

In this context, a critical analysis of the pros and cons of membrane separation processes in a post-combustion capture framework, in light of new material developments, is of interest and is proposed hereafter.

Additionally, different types of design possibilities for membrane processes (single stage, multistage, hybrid process) shown in Figure 1 will be discussed in the next sections. However, the emphasis will be put on a single stage membrane process design.

1 MEMBRANES AND POST-COMBUSTION CARBON CAPTURE: FRAMEWORK

Schematically, the analysis of gas separation membrane processes for CO₂ capture depends on two different types of factors, which will be detailed in the next sections:

- a materials science aspect which addresses the evaluation of the intrinsic separation performances of the membrane. This topic typically requires the structure and/or the mass transfer mechanism(s) taking place in the membrane to be determined;

- a process engineering science aspect, which aims at the determination of the best design and operating conditions for a given membrane material. Classical tools of chemical engineering and separation science are used for this purpose.

Combining materials and process engineering considerations, the energy requirement and the size of the installation, the two key data of technico-economical studies, can be finally obtained (Zolandz and Fleming, 1995).

Generally speaking, the interplay between material and process engineering is a key feature of membrane science. Unfortunately, for CO₂ capture, these two domains are often disconnected: numerous publications report only on material structure and performances, while process design studies sometimes ignore the specificities of membrane materials. The two main objectives of the carbon capture step are the CO₂ purity level (noted y hereafter) and the capture ratio (noted R and usually fixed at 0.9 for post-combustion studies, Deschamps and Pilavachi, 2004). The capture ratio of a single stage membrane unit (Fig. 1a) is obtained through:

$$R = \theta \cdot y/x_{in} \quad (1)$$

with the stage-cut (θ), corresponding to the fraction of the feed flow (Q_{in}) which effectively permeates through the membrane on the permeate side (Q_p), expressed as:

$$\theta = \frac{Q_p}{Q_{in}} \quad (2)$$

Any membrane separation process requires a driving force to operate, classically expressed through the pressure ratio, which corresponds to the ratio of the downstream over upstream pressure:

$$\psi = \frac{p''}{p'} \quad (3)$$

CO₂ purity (y) logically depends on the feed composition and the material performances, namely the membrane selectivity α ; α is determined from the ratio of the CO₂ permeability over N₂ permeability under steady state conditions. In a large majority of cases, only the experimental permeabilities of the pure compounds are known, leading to the so-called ideal selectivity of the material:

$$\alpha^* = \frac{P_i}{P_j} \quad (4)$$

It is important to note that the effective purity produced by a membrane unit does not depend only on the

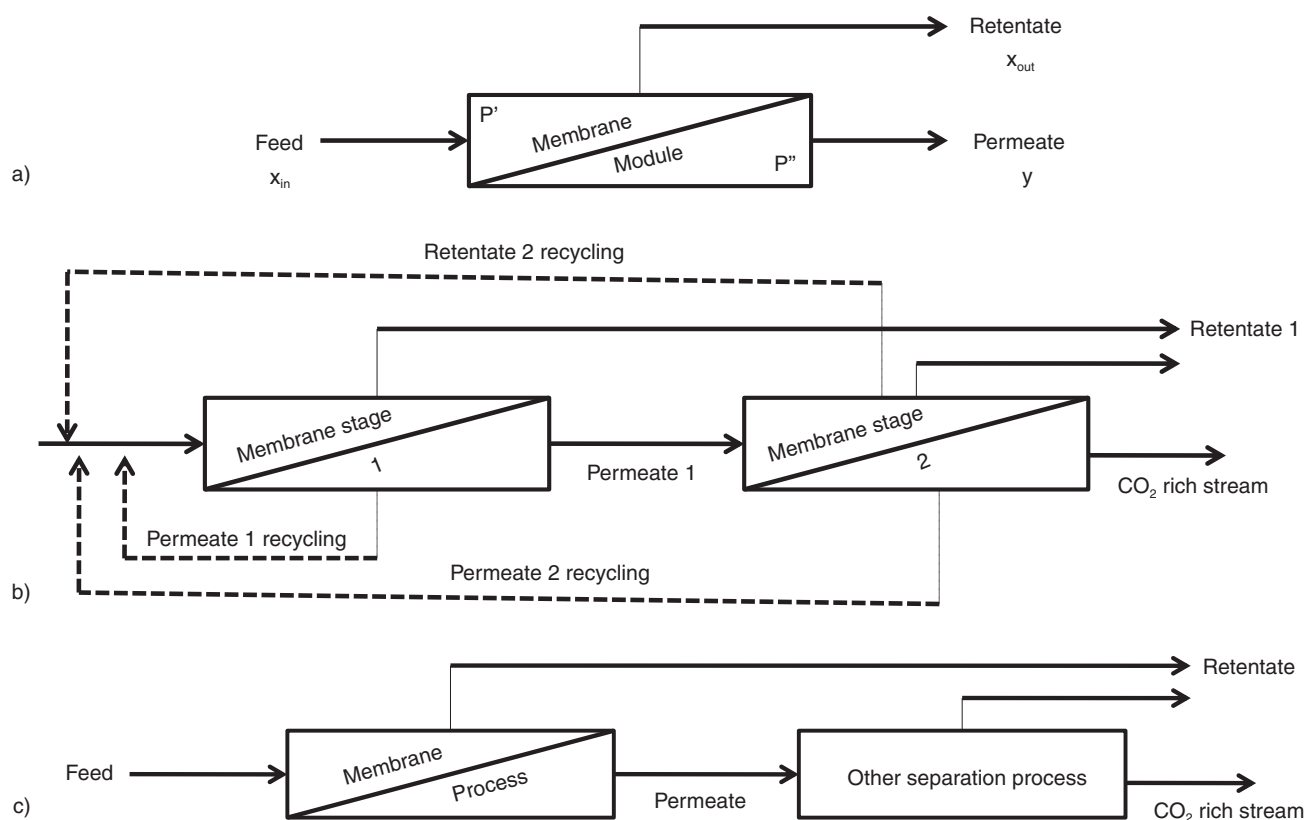


Figure 1

Schematic representation of different process flowsheet possibilities for membranes in post-combustion: a) single stage membrane module, b) multistage membrane process, c) hybrid process combining a membrane module as a first concentration step and another separation process as a polishing step.

membrane selectivity, but is also affected by the module operating conditions, especially the pressure ratio (Ψ). Additionally, the capture ratio (R) also affects the purity level, due to mass balance constraints. This qualitative analysis illustrates how material and process variables are closely interconnected, as discussed hereafter.

2 MEMBRANE MATERIALS FOR CO₂ CAPTURE: STATE OF THE ART

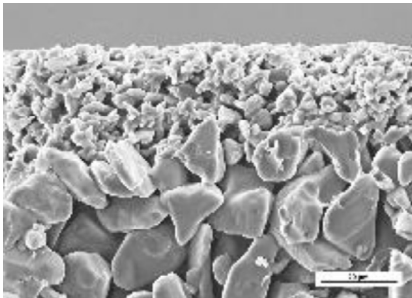
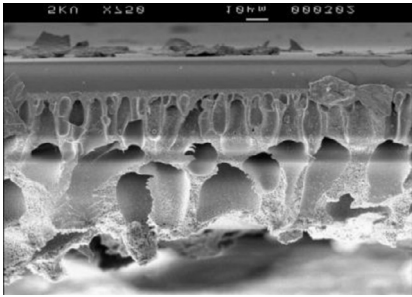
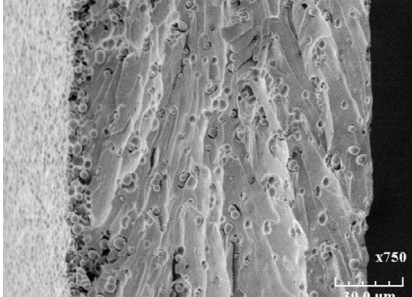
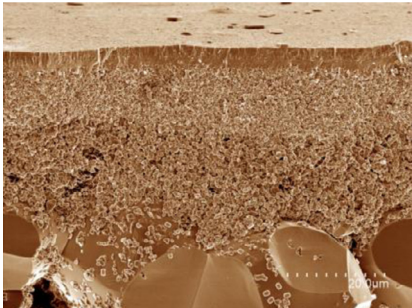
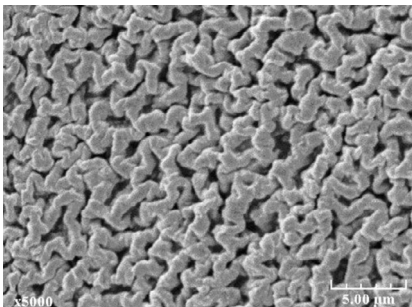
A very large number of membrane materials has been investigated for gas separation applications for decades. In terms of industrial applications however, a very limited number of materials, almost exclusively polymers, is used. For CO₂ capture, a great number of studies have been reported on different materials such as polymeric, inorganic, hybrid organic-inorganic and facilitated transport membranes (Ebner and Ritter, 2009;

Luis *et al.*, 2012). Depending on the material characteristics, different transport mechanisms for the gaseous compounds (*i.e.* CO₂ and N₂ for post-combustion capture studies) summarized in Table 1, can take place (Koros, 1993; Baker, 2004).

For a given separation (such as CO₂/N₂ in post-combustion), a membrane material should ideally combine two target performances (Zolandz and Fleming, 1995):

- a high selectivity (*i.e.* ratio of the two compounds steady state permeability, Eq. 4), in order to achieve the purity target, ideally in a single stage process;
- a high permeability, in order to minimize the surface area required for a given application. Permeability of a dense polymeric material is usually expressed in Barrer, the most common unit, and the ratio of the permeability to the membrane thickness, usually named permeance is the most relevant characteristics for engineering calculation. For membrane gas

TABLE 1
 Different types of membrane materials and corresponding separation mechanisms

Material type	Example	Separation mechanism
Microporous inorganic membrane (silica, carbon, etc.) with pore diameter ranging between permeants kinetic diameter and mean free path		Knudsen flow Very low selectivity for CO ₂ /N ₂
Dense skin polymeric membrane		Solution-diffusion, upper performances predictable by trade-off analysis. Industrial membrane gas separations make use of this type of materials
Mixed Matrix Membranes (continuous polymeric phase with dispersed inorganic adsorbing particles)		Hybrid mechanism: solution-diffusion + surface flow, possibility to overpass trade-off limitations
Zeolite or molecular sieve membrane (pore diameter close to or smaller than molecules kinetic diameter)		Molecular sieving, very high selectivity theoretically achievable providing that defect free materials can be produced at a large scale
Liquid Membranes (LM), Fixed Site Carrier Membranes (FSCM): liquid impregnated in a porous membrane or dissolved in a dense polymer		Reaction with a mobile or fixed carrier molecule + diffusion in a liquid. High selectivity achievable. Usually requires water

separations, permeance is often expressed in GPU (Gas Permeation Unit).

An overview of the main different materials investigated for CO₂/N₂ separation and their performances are summarized in Tables 2-5. Selectivity and permeance are often antagonistic and an inverse relationship is obtained when they are simultaneously reported on a graph (Robeson Lloyd, 2008). Figure 2 presents the CO₂/N₂ selectivity (α) data for different membrane materials *versus* CO₂ permeance. The trade-off curve, obtained

through theoretical calculation and specific to dense polymers only, has been added (Freeman, 1999). The most relevant advances in each class of membrane materials; polymeric, inorganic, hybrid organic-inorganic and facilitated transport membranes are detailed hereafter.

2.1 Polymeric Membranes

Commercial gas separation membranes include mainly: polyimide, polysulfones, polycarbonates, polyphenyl

TABLE 2
Selected high performing membrane materials-data for dense polymeric membranes

	CO ₂ /N ₂ selectivity (α)	Membrane CO ₂ permeance (GPU)	Membrane	Reference
Polymers of intrinsic microporosity (PIMs)	25	>12 000*	Polybenzodioxanes PIM-1	Budd <i>et al.</i> (2008)
Polymers of intrinsic microporosity (PIMs)	40	2 000*	PIM-1 modified: tetrazole-functionalized	Du <i>et al.</i> (2011)
Composite	50	1 000	Polaris TM Thin Film Composite (TFC) + selective layer similar to Pebax	Merkel <i>et al.</i> (2010)
Block copolymers	75	1 000	Poly(ethylene oxide) poly(butylenes terephthalate) block copolymers	Metz <i>et al.</i> (2004)
Block copolymers	60	1 850	Polyactive: copolymer: poly(ether-block-ester)	Yave <i>et al.</i> (2010a); Liu <i>et al.</i> (2005)
Block copolymers	58	>500	Poly(trimethylene terephthalate)-block-poly(ethylene oxide) (PTT-b-PEO) copolymers	Yave <i>et al.</i> (2010b)

* Indicates that CO₂ permeance is estimated from membrane permeability, assuming a 1 μ m dense layer thickness.

TABLE 3
Selected high performing membrane materials – data for inorganic and hybrid organic-inorganic membranes

Membrane type	CO ₂ /N ₂ selectivity (α)	Membrane CO ₂ permeance (GPU)	Membrane	Reference
Zeolites	>500	300	Faujasite or zeolite Y membrane on alumina support	White <i>et al.</i> (2010)
Zeolites	200	200 000	NAY zeolite membrane (molecular simulation data)	Krishna and van Baten (2012)
Zeolites	69	2 100	Zeolite membranes	Ebner and Ritter (2009)
Silicas	50	900	Pure microporous silica membrane	Xomeritakis <i>et al.</i> (2007)

TABLE 4
Selected high performing membrane materials – data for hybrid organic-inorganic membranes

Membrane type	CO ₂ /N ₂ selectivity (α)	Membrane CO ₂ permeance (GPU)	Membrane	Reference
MOFs	30	>30 000	MgMOF-74, theoretical value, $e = 50 \mu\text{m}$	Krishna and van Baten (2012)
Mixed matrix membrane	72	154	(PEBAX)-Silica (90:10)	Kim and Lee (2001)
Mixed matrix membrane	118	205	PEBAX-Silica (81:19)	Kim and Lee (2001)
Mixed matrix membrane	79	277	PEBAX-Silica (73:27)	Kim and Lee (2001)

TABLE 5
Selected high performing membrane materials – data for facilitated transport membranes

Membrane type	CO ₂ /N ₂ selectivity (α)	Membrane CO ₂ permeance (GPU)	Membrane	Reference
Fixed Site Carrier Membranes (FSCM)	150	>300	Polyvinyl amine (PVAm) and polyvinyl alcohol (PVA) blend membrane. Selective layer thickness of 0.3-0.7 μm	Deng <i>et al.</i> (2009) ; Deng and Hägg (2010) ; Matsuyama <i>et al.</i> (1999)
Fixed Site Carrier Membranes (FSCM)	120	320	Fixed carrier in a solvent-swollen membrane Water-swollen chitosan (poly(D) glucosamine) membrane	El-Azzami and Grulke (2008)
Fixed Site Carrier Membranes (FSCM)	500	>6 000 B	Poly (allylamine) as a fixed carrier 2-aminoisobutyric acid-potassium salt as a mobile carrier in a crosslinked PVA matrix	Huang <i>et al.</i> (2008)
Fixed Site Carrier Membranes (FSCM)	500	840	Composite membranes (coating PPO and PSF with high molecular PVAm)	Sandru <i>et al.</i> (2010)
Fixed Site Carrier Membranes (FSCM)	>500	>1 800	PVAm composite membranes with PH control	Kim <i>et al.</i> (2013)
Fixed Site Carrier Membranes (FSCM)	800	300	Amine-modified mesoporous silica membranes	Barillas <i>et al.</i> (2011)
Liquid membrane	200	100	DEA supported on poly (vinyl alcohol) membranes	Francisco <i>et al.</i> (2010)
Liquid membrane	820	52	Enzyme supported on polymer	Zhang <i>et al.</i> (2010)

oxides, cellulose derivatives and poly(ethylene oxide) (Ebner and Ritter, 2009; Luis *et al.*, 2012). Numerous studies are reported on polymeric membrane materials attempting to improve their performances for CO₂/N₂ separation, which logically almost systematically fall below the trade-off curve (*Fig. 2*). For dense polymers, a composite membrane based on a segmented block copolymer (PolarisTM), a type of poly(ethylene oxide)

co-polymer, has been specifically designed for carbon capture applications up to the industrial scale (spiral wound modules) ([Merkel *et al.*, 2010](#)). This material shows a CO₂ permeance of 1 000 GPU with a CO₂/N₂ selectivity of 50. Another example of block copolymers is poly(ethylene oxide) poly(butylenes terephthalate) block copolymers with a selectivity of 75 and a CO₂ permeance of 1 000 GPU ([Metz *et al.*, 2004](#)). Up to day, these

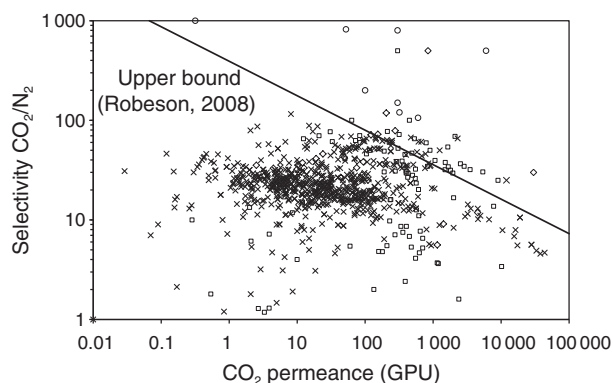


Figure 2

Trade-off curve showing the CO_2/N_2 selectivity (α) data for different membrane materials *versus* CO_2 permeance for a 1 m thick membrane, x : polymeric membranes, □ : inorganic membranes, ○ : facilitated transport membranes, ◇ : hybrid organic-inorganic membranes. The theoretical trade-off limit, calculated for a strict physical separation mechanism through a dense polymer (*i.e.* solution-diffusion is also shown).

performances can be considered as the upper limit for dense polymeric membranes based on a physical separation mechanism.

2.2 Inorganic Membranes

Inorganic membranes are very attractive because they can potentially show better performances and resistance against high temperature and pressure conditions in comparison to polymeric membranes. Classical materials include carbon, alumina, zeolites and silicas (Ebner and Ritter, 2009). Two outstanding results have been recently reported for CO_2/N_2 separation on tailor made materials at lab scale. A selectivity of 200 and permeance of 200 000 GPU has been obtained based on molecular sieve separation mechanism with a NAY zeolite membrane (Krishna and van Baten, 2011). A higher selectivity of 500 and a CO_2 permeance of 300 GPU have been reported with another type of zeolite membrane (White *et al.*, 2010). It can be seen in Figure 2 that these performances stand far above the trade-off curve of dense polymers.

2.3 Hybrid Organic/Inorganic Membranes

These membranes consist of mixtures of organic and inorganic phases. Classically, inorganic particles (adsorbents) are dispersed into a dense polymeric matrix (Tab. 4). The corresponding material is often named Mixed Matrix Membrane (MMM). This strategy offers

the possibility to overcome the permeability/selectivity trade-off of polymeric membranes, as shown in Figure 2. The dispersed inorganic phase, which may consist of various types of materials (silicas, zeolite), may act as a molecular sieve or as a Selective Surface Flow (SSF) material. In other cases, the two phases interactions can open inter-chain distance improving both selectivity and permeability. The inorganic phase can also improve both the mechanical and thermal resistance of the polymeric phase. New organic-inorganic hybrid materials based on metal cation sites in porous crystalline phase have also been developed. This class of adsorbent particles is called Metal Organic Frameworks (MOF). Molecular simulations have recently been reported with the possibility to get MgMOF-74 membranes with a permeance greater than 30 000 and a selectivity of about 30 (Krishna and van Baten, 2012) higher selectivity of about 118 is reported for a mixed matrix membrane based on PEBAX-Silica (81:19) with a CO_2 permeance of 205 GPU (Kim and Lee, 2001).

2.4 Facilitated Transport Membranes (FTM)

Facilitated Transport Membranes (FTM) are based on a selective reversible reaction between the incorporated carrier agents and the target gas component. It should be stressed that for these membranes the transport is different from the solution-diffusion mechanism which takes place in dense polymeric membranes. These membranes are known to show high selectivities together with high fluxes (Ebner and Ritter, 2009; Luis *et al.*, 2012; Ramasubramanian and Winston Ho, 2011; Xomeritakis *et al.*, 2005). They can be divided into two categories: Fixed Site Carrier Membranes (FSCM) where the carriers are chemically bonded to the polymer and mobile site carrier membranes, usually named Liquid Membranes (LM) where the carrier can diffuse in the membrane. The two membrane categories have shown attracting performances for CO_2/N_2 mixture. Recently, a permeability above 6 000 Barrer and a selectivity of about 500 has been reported for a membrane based on poly (allylamine) as a fixed carrier and 2-aminoisobutyric acid-potassium salt as a mobile carrier in a crosslinked PVA matrix (Huang *et al.*, 2008). One peculiarity of FSCM and LM is to require water for the selective reaction towards CO_2 to take place; this constraint does not hold for the other membrane materials. Consequently, the separation performances of reactive membranes strongly depend on humidity and a certain level of hydration has to be maintained on the two sides of the membrane for correct operation. More precisely, a classical operation with vacuum pumping on the downstream side is the more favorable possibly

with 1.5-3 bar feed pressure, and 200-300 mbar vacuum. The carriers in FTM will become saturated quicker if compression strategy is used on feed side. This specificity logically has a strong impact on process design features.

The overview of membrane characteristics and performances described above shows that impressive improvements have been recently achieved for the CO₂/N₂ separation challenge (Ramasubramanian and Winston Ho, 2011). It should be stressed however that most studies concern sample materials tested at the lab scale, with pure gases, leading to ideal selectivity data; experiments with gas mixtures and/or humid feeds, in order to better mimic real flue gas conditions, are scarce. Up to now only one tailor made material, the composite Polaris membrane based on a dense polymeric skin, has been tested, including membrane module development, up to the pilot scale on real flue gases (Merkel *et al.*, 2010). The evaluation of the interest of more selective and/or permeable materials is obviously a key issue for materials development purposes; this target is best evaluated through simulation studies. Process design characteristics of membrane separation will now be detailed.

It is important to note that the simulation framework used in this study does not hold for FTM membranes because of the specificity of their transport mechanism as mentioned in Section 2.4 (permeability and selectivity constancy).

3 SINGLE STAGE MEMBRANE PROCESS DESIGN FOR CO₂ CAPTURE APPLICATIONS

The simulation of membrane based gas separations has been investigated for decades and the possibility to correctly predict the separation performances of a unit through a series of key equations and associated assumptions is abundantly documented (Bounaceur *et al.*, 2006; Kaldis *et al.*, 2000; Chowdhury *et al.*, 2005; Coker *et al.*, 1999; Matson, 1983; Zanderighi, 1996). Similarly to numerous studies in this field, a cross-plug flow model has been used for the simulations shown in this section. Models assumptions and mathematical model have been presented in details in our previous work (Favre, 2007). The performances of the separation can be simulated based on numerical resolution using the DASSL (Differential/Algebraic System Solver) method (Bounaceur *et al.*, 2006; Petzold, 1983).

Like any process design study, a series of variables has first to be defined; in a second step, a fixed number of unknowns can be identified through analytical or numerical resolution. For carbon capture studies, two

key constraints, detailed before, are imposed: the CO₂ capture ratio ($R = \theta \times (y/x_{in})$) corresponding to the fraction of inlet CO₂ recovered in the permeate stream and the CO₂ purity produced at the permeate side (y).

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

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

For post-combustion applications, the permeate flux of each compound is assumed to result from its own driving, flux coupling effects being negligible (Scholes *et al.*, 2010; Hughes and Jiang, 1995; Dhingra and Marand, 1998). The influence of these different variables will be discussed hereafter, through a series of simulations, in link with the materials performances detailed in the previous section. For all simulations, the feed gas stream of the membrane module has been considered to be a binary dry CO₂/N₂ mixture at 30°C and under atmospheric pressure.

3.1. Interplay Between Pressure Ratio and Membrane Selectivity for a Target CO₂ Purity

In a first step, the interplay between the membrane material performances and process operating conditions is illustrated. More specifically, the influence of pressure ratio and membrane selectivity is investigated through an illustrative example for a single stage module. Results are shown in Figure 3. The permeate purity (y) is shown as a function of the pressure ratio (ψ) for different inlet CO₂ content ($x_{in} = 0.05$ typical of a gas turbine, $x_{in} = 0.15$ corresponding to coal combustion, and $x_{in} = 0.3$ for oxygen enriched air combustion) (Lie *et al.*, 2007; Hendriks *et al.*, 2009); CO₂ recovery ratio is fixed at 90%. The results are given for different membrane selectivity of $\alpha = 50, 100$ and 200, in order to cover the range of materials selectivity performances detailed in the previous section.

First, one can remark that the required pressure ratio decreases as the desired permeate CO₂ purity increases. This induces an increased energy requirement when a higher purity target is fixed. Besides, high membrane selectivity logically permits to attain high permeate purity, for a given pressure ratio.

Also, it can be seen that at low pressure ratios (high driving force), the pressure ratio limitation is reduced and the role of membrane selectivity becomes important

(Merkel *et al.*, 2010; Bounaceur *et al.*, 2006). Generally, as the pressure ratio decreases, the benefit from higher membrane selectivity increases.

Moreover, it can be seen that for a given permeate purity, the pressure ratio decreases with increasing the inlet CO₂ mole fraction (x_{in}). Consequently, when low inlet CO₂ concentrations are to be treated and when high permeate CO₂ purity is desired, the membrane selectivity

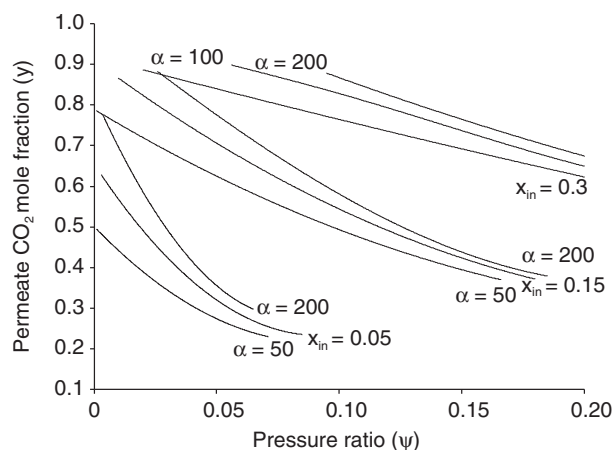


Figure 3

Permeate CO₂ mole fraction as a function of membrane pressure ratio for different inlet CO₂ concentrations ($x_{in} = 0.05-0.15-0.3$) and different membrane selectivity ($\alpha = 50-100-200$). $R = 0.9$.

will play a key role and energy requirement will strongly increase (Belaïssaoui *et al.*, 2012a).

More concretely, for a classical 0.9 purity target and 0.15 CO₂ inlet content (the most frequent flue gas composition), it can be noticed that a high selectivity level (around 200) is needed. Coming back to Tables 2-5 and Figure 2, one can notice that dense polymeric materials will not enable this target to be attained. As a consequence, multistage processes are needed in that case (Belaïssaoui *et al.*, 2012a). At this stage, it can be concluded from the materials point of view that the possibility to reach high selectivity levels through non polymeric membranes (Tab. 3-5) could be attractive because it offers the possibility to theoretically use a single stage unit for coal power plants.

3.2. Compression Strategy and Energy Requirement

It is important to note that, for a given pressure ratio such as shown in Figure 3, several possibilities are offered in terms of operating conditions. The choice between these options can be made, among others, with respect to the energy requirement, the main process selection constraint of carbon capture challenge. The driving force strategy adopted to achieve the pressure ratio across the membrane can indeed be generated by feed compression and/or permeate vacuum pumping and/or gas sweeping. Figure 4 shows a schematic diagram of these configurations.

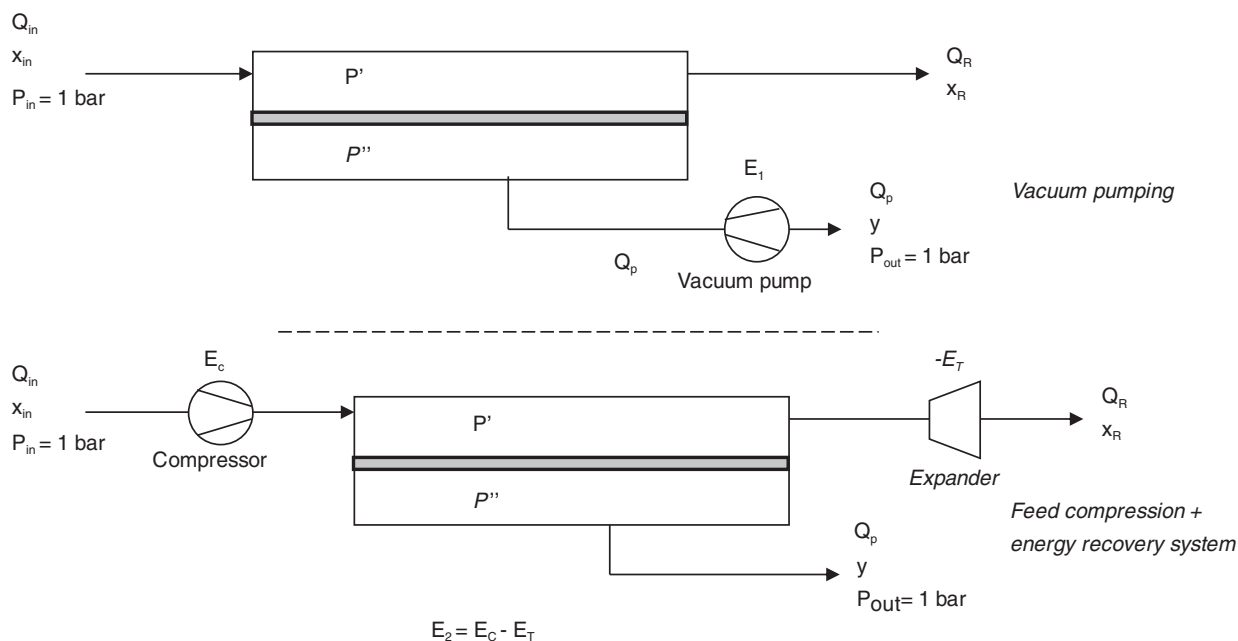


Figure 4

Schematic representation of the different compression strategies of a single stage membrane unit for post-combustion CO₂ capture.

TABLE 6
Expressions used for the calculation of the energy requirement (E) for the configurations shown in Figure 4

Compression strategy	Expression of the specific energy in GJ/ton of recovered CO ₂ (thermal basis)	
Vacuum pumping	$E_1 = 2.7 \times 10^{-3} \frac{1}{\eta_v(\Psi)} \frac{1}{xM(\text{CO}_2)} \frac{\gamma RT}{\gamma - 1} \left[\left(\frac{1}{\Psi} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right]$	(5)
	η_v : Vacuum pump efficiency (Matsumiya <i>et al.</i> , 2005): $\eta_v(\Psi) = 0.1058 \times \ln(\Psi) + 0.8746$	
Feed compression with energy recovery in the retentate	$E_2 = E_C - \eta_E \times 2.7 \times 10^{-3} \times \left(\frac{1}{\theta} - 1 \right) \times \frac{1}{xM(\text{CO}_2)} \frac{\gamma RT}{\gamma - 1} \left[\left(\frac{1}{\Psi} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right]$	(6)
	$E_C = 2.7 \times 10^{-3} \frac{1}{\eta_C} \frac{1}{yM(\text{CO}_2)\theta} \frac{\gamma RT}{\gamma - 1} \left[\left(\frac{1}{\Psi} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right]$	(7)
	η_E : expander efficiency = 0.90 η_C : compressor efficiency = 0.90 (Zhao <i>et al.</i> , 2008, 2010; Van der Sluijs <i>et al.</i> , 1992)	

Generally, three major options can be proposed:

- a direct feed compression strategy is most often selected for gas separations but, for carbon capture, it corresponds to the largest energy requirement because the total feed flowrate has to be compressed (Merkel *et al.*, 2010; Bounaceur *et al.*, 2006);
- a vacuum pumping strategy is recommended when a minimal energy requirement is necessary. In that case, a smaller flowrate, namely the permeate flowrate, has to be pumped. For a stage cut of 0.1, the energy requirement will be in principle ten times lower than the direct compression strategy. This option shows however several drawbacks: vacuum operation can be difficult at large scale, vacuum pumps energy efficiency can be much lower than compressors. Furthermore, the surface area will be much larger than that required for direct compression because of the lower driving force generated;
- a third possibility, consists to use an Energy Recovery System (ERS) at the retentate exit (high pressure side) of a direct compression unit. In that case, energy requirement can be close to vacuum pumping and surface requirement will correspond to direct compression. This interesting trade-off demands however an increased capital cost (*i.e.* ERS).

The calculation of the energy requirement of each two last strategies is detailed in Table 6.

Figure 5 illustrates the above considerations; the aggregate membrane surface area and the energy needed for vacuum pumping and compression with an ERS, such as turbo-expander are compared. The results are presented for $x_{in} = 0.3$, a membrane selectivity of 100, CO₂ permeance of 1 000 GPU and CO₂ permeate purity of 0.9. Energy requirement, first

obtained from the electrical power of the compressor or vacuum pump, is converted in GJ per tonne of CO₂ captured, on a thermal basis (with a 2.7 work/heat factor), in order to enable a comparison with amine absorption processes. One may note that the two strategies lead to values which are similar, the vacuum pumping energy requirement being slightly lower for lower values of the recovery ratio. Nevertheless, it should be stressed that the feed compression strategy leads to a significantly lower membrane surface area than that required for the vacuum pumping strategy.

This analysis illustrates the compromise existing between energy requirement and membrane surface. It suggests the existence of an optimal recovery ratio for each strategy with a minimum total cost that could be determined with a technico-economical analysis.

3.3. Synthesis: Membrane Selectivity, Permeate Purity and Energy Requirement

The strong interaction between membrane selectivity, inlet CO₂ concentration, CO₂ purity and energy requirement has been discussed above. The combined relationship between these key variables is shown in Figure 6. The energy requirement (GJ/ton thermal basis) of a single stage membrane unit with feed compression + ERS is shown as a function of the permeate purity for different inlet CO₂ content of $x_{in} = 0.05, 0.15$ and 0.3 and CO₂ recovery ratio of 90%. The results are given for different membrane selectivity of $\alpha = 50, 100$ and 200 .

In this figure, the benefit of higher membrane selectivity in reducing the energy requirement of the single stage membrane process is highlighted. Nevertheless, taking into account 2 GJ/ton as a key target for energy

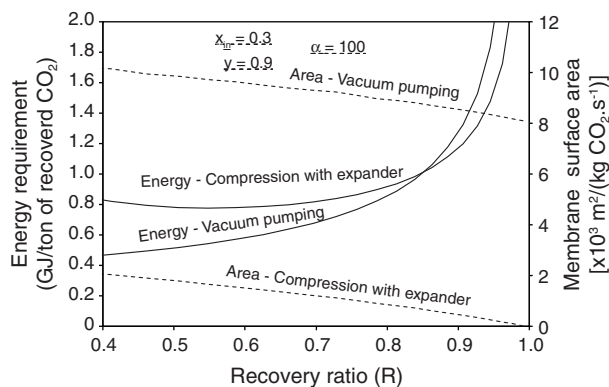


Figure 5

Illustrative comparison of the compression + expander and vacuum pumping strategies. Energy and membrane area as a function of CO₂ recovery ratio. Results are presented for two compression strategies:

- compression with turbo-expander ERS,
- vacuum pumping (or permeate vacuum).

Results for $x_{in} = 0.3$ and membrane selectivity of 100.

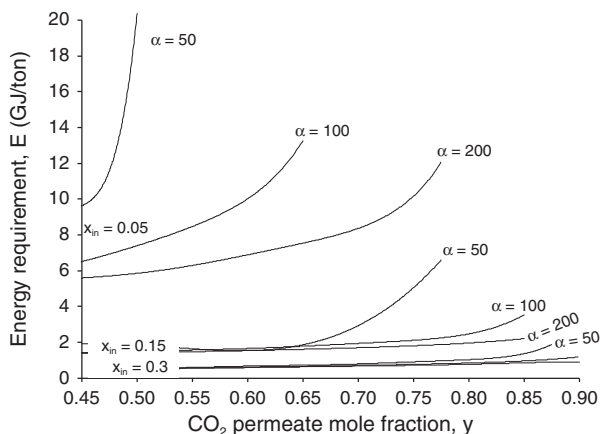


Figure 6

Energy requirement as a function of permeate CO₂ purity for different inlet CO₂ concentration ($x_{in} = 0.05-0.15-0.3$) and different membrane selectivity ($\alpha = 50-100-200$). $R = 0.9$.

requirement, it can be concluded that a single stage membrane unit does not offer attractive performances for gas turbines ($x_{in} = 0.05$), whatever the material selectivity level. Clearly, alternative approaches such as hybrid or integrated systems are thus required for membrane implementation on gas turbines.

For coal combustion ($x_{in} = 0.15$), energy requirement limitations restrict permeate purity to be limited to 0.65 with a membrane selectivity of 50 (a typical performance of dense polymeric membranes). This limitation again suggest multistage or hybrid systems to be applied. With higher selectivities (such as 100 or 200, potentially achievable by fixed site carrier membranes or inorganic membranes), permeate purity can reach 0.85. This level is often considered to be too low for compression and transportation. A second membrane stage or polishing process remains probably necessary.

Finally, a single stage membrane unit offers attractive performances when inlet CO₂ content is around 0.3. From the energy requirement point of view, there is no need for highly selective membranes in that case. This situation is however rather uncommon in post-combustion, expect special emissions (biogas, cement, etc.) (Sheinbaum and Ozawa (1998)) or oxygen enriched air combustion.

It is worth to note that the simulated reported in this section are based on dry binary feed gas mixture CO₂/N₂. The influence of the other gas component in the flue gas *e.g.* should be taken into account. Indeed, more complex process design and/or lower efficiency can result

from the presence of O₂ and H₂O (Zha and Rubin, 2013; Franz *et al.*, 2013; Low *et al.*, 2013).

4 SYNTHESIS AND CONCLUDING REMARKS

The materials and process design issues of membrane for post-combustion carbon capture have been presented and discussed above. In summary, it can be stated that despite impressive materials improvements in membrane selectivity and/or permeance, it is impossible to attain carbon capture specifications with a single stage membrane unit for the large majority of flue gases (gas turbines and coal power plants). Consequently, while numerous design studies focus on the single stage situation (Fig. 1a), there is a crucial need to tackle more complex systems such as multistage (Fig. 1b) (Merkel *et al.*, 2010) or hybrid processes (Fig. 1c) (Favre *et al.*, 2009; Belaisaoui *et al.*, 2012c). Compared to the single stage case, these systems show a large number of variables, combined to numerous architecture possibilities (such as recycling loops). It is important to notice that a simple two stage membrane process without recycling loops cannot compete to amine absorption in terms of energy requirement, even with a CO₂/N₂ selectivity of 100 (Skorek-Osikowska *et al.*, 2013). This observation shows that more sophisticated designs have to be explored for multistage membrane units. Unfortunately, very few studies addressed these problems up to now with the carbon capture constraints (Bhown and Freeman, 2011), as indicated by the limited

TABLE 7
Overview of key process design studies publications on multistage membrane (2 stages) processes for post-combustion capture

Feed condition	Process conditions and membrane parameters	Reference
14% CO ₂	Feed compression CO ₂ /N ₂ = 19-43 $\rho_{CO_2/z}$ = 61-375 GPU	Van der Sluijs <i>et al.</i> (1992)
13% CO ₂	Feed compression/vacuum pumping α_{CO_2/N_2} = 20-800 $\rho_{CO_2/z}$ = 200-1 000 Barrer	Ho <i>et al.</i> (2008)
15% CO ₂	Feed compression Retentate recycle	Herzog (1991)
15% CO ₂	Vacuum α_{CO_2/N_2} = 100	Kotowicz and Bartela (2012), Skorek-Osikowska <i>et al.</i> (2013)
10% CO ₂	Feed compression/vacuum pumping α_{CO_2/N_2} = 50 $\rho_{CO_2/z}$ = 1 000 GPU	Merkel <i>et al.</i> (2010)
14% CO ₂	Feed compression/vacuum pumping α_{CO_2/N_2} = 10-200 $\rho_{CO_2/z}$ = 182.75-1 827.5 GPU	Zhao <i>et al.</i> (2010)

TABLE 8
Overview of key process design studies publications on hybrid processes including a membrane unit for post-combustion capture

Feed condition	Process conditions and membrane parameters	Reference
Methane combustion	Flue gas recycle with an oxygen enriched feed mixture and CO ₂ capture by membranes α_{CO_2/N_2} = 50-200 Feed compression	Favre <i>et al.</i> (2009)
5 to 30% CO ₂	Hybrid membrane cryogenic separation for CO ₂ capture	Belaissaoui <i>et al.</i> (2012c)
Natural gas turbine	Combicap: interconnected gas turbines with membrane CO ₂ capture unit and integrated combustor-heat exchange system	Lynghjem <i>et al.</i> (2004)
15% CO ₂	Membrane / PSA hybrid process	Jeon <i>et al.</i> (2004)

number of references in Table 7. A summary of the publications recently published for hybrid systems including one membrane separation step, with some key characteristics, is provided in Table 8. For each of these studies, a certain number of variables such as material performances or operating conditions has necessarily to be fixed among the numerous variables which have to be taken into account; consequently an holistic analysis of the situation is far to be achieved and a critical comparison and synthesis is extremely difficult. Similarly to other carbon capture process studies, the overall energy requirement of the system usually logically remains the objective variable number

one. Nevertheless, it should be stressed that taking the energy requirement as the only objective variable can generate erroneous conclusions. A capture unit has also to attain the purity and recovery targets, and, more importantly, it has to be economically competitive.

Consequently, the ultimate and most relevant objective function of design studies should ideally be the effective cost of the capture unit, to be compared to other technologies. Unfortunately, the number of technico-economical analyses on membranes for post-combustion capture is extremely limited (Merkel *et al.*, 2010; Herzog, 1991; Van der Sluijs *et al.*, 1992; Zhao *et al.*, 2008;

Ho *et al.*, 2006, 2008). Given the uncertainties on key variables such as the membrane cost and/or lifetime, it is almost impossible to propose today a clear vision on the potential of membrane separation units for post-combustion carbon capture.

In conclusion, membrane separations for post-combustion carbon capture have not been investigated for a long time and they attracted attention only recently compared to gas-liquid absorption technology. Despite tremendous efforts and impressive improvements in the performances of membrane materials, the best place and role of membrane units remain unclear. Multistage or hybrid systems, integrated solutions probably offer the most promising solutions but these aspects are largely unexplored up to now. Nevertheless, promising results have been recently reported on experiments with real flue gases treatment at a pilot scale in two pioneering projects (Merkel *et al.*, 2010; Hagg *et al.*, 2012; Sandru *et al.*, 2012). In that context, the priority of research should be to promote design studies for multistage and/or hybrid systems, coupled to an economical analysis. Based on this, a better view of the target selectivity/permeance performances of membrane materials which fit the carbon capture constraints could be achieved. These objectives and developments, ideally combining material science, chemical engineers and power plant experts are an essential issue in order to unambiguously evaluate the potentialities of what could be a key process piece of second stage carbon capture processes.

REFERENCES

- Baker R. (2004) Membrane technology and applications, J. Wiley, Chichester, New York.
- Barillas M.K., Enick R.M., O'Brien M., Perry R., Luebke D. R., Morreale B.D. (2011) The CO₂ permeability and mixed gas CO₂/H₂ selectivity of membranes composed of CO₂-philic polymers, *Journal Membrane Science* **372**, 1-2, 29-39.
- Belaissaoui B., Willson D., Favre E. (2012a) Membrane gas separations and post-combustion CO₂ capture: parametric sensitivity and process integration strategies, *Chemical Engineering Journal* **211-212**, 122-132.
- Belaissaoui B., Cabot G., Cabot M.S., Willson D., Favre E. (2012b) An energetic analysis of CO₂ capture on a gas turbine combining flue gas recirculation and membrane separation, *Energy* **38**, 167-175.
- Belaissaoui B., Le Moullec Y., Willson D., Favre E. (2012c) Hybrid Membrane cryogenic process for post-combustion CO₂ capture, *Journal Membrane Science* **415-416**, 424-434.
- Bhown A.S., Freeman B.C. (2011) Analysis and status of post-combustion carbon dioxide capture technologies, *Environmental Science Technology* **45**, 8624-8632.
- Bounaceur N., Lape N., Roizard D., Vallières C., Favre E. (2006) Membrane processes for post-combustion carbon dioxide capture: a parametric study, *Energy* **31**, 2556-2570.
- Budd P.M., McKeown N.B., Ghanem B.S., Msayib K.J., Fritsch D., Starannikova L., Belov N., Sanfirova O., Yampolskii Y., Shantarovich V. (2008) Gas permeation parameters and other physicochemical properties of a polymer of intrinsic microporosity: Polybenzodioxane PIM-1, *Journal Membrane Science* **325**, 851-860.
- Chowdhury M.H.M., Feng X., Douglas P., Croiset E. (2005) A new numerical approach for a detailed multicomponent gas separation membrane model and Aspen plus simulation, *Chemical Engineering Technology* **28**, 773-782.
- Coker D.T., Allen T., Fleming G.K. (1999) Nonisothermal model for gas separation hollow fiber membranes, *AIChE Journal* **45**, 1451-1468.
- Davidson O., Metz B. (2005) Special Report on Carbon Dioxide Capture and Storage, International Panel on Climate Change, Geneva, Switzerland, (www.ipcc.ch).
- Deng L., Hägg M.B. (2010) Swelling behavior and gas permeation performance of PVAm/PVA blend FSC membrane, *Journal Membrane Science* **363**, 1-2, 295-301.
- Deng L., Kim T.-J., Hagg M.-B. (2009) Facilitated transport of CO₂ in novel PVAm/PVA blend membrane, *J. Membrane Sci.* **340**, 154-163.
- Deschamps P., Pilavachi P.A. (2004) Research and development actions to reduce CO₂ emissions within the European Union, *Oil Gas Science Technology* **59**, 3, 323-30.
- Dhingra S., Marand E. (1998) Mixed gas transport study through polymeric membranes, *Journal Membrane Science* **141**, 45-63.
- Du N., Park H.B., Robertson G.P., Dal-Cin M.M., Visser T., Scales L., Guiver M.D. (2011) Polymer nanosieve membranes for CO₂-capture applications, *Nature Materials* **10**, 372-375.
- Ebner A.D., Ritter J.A. (2009) State, state-of-the art adsorption and membrane separation processes for carbon dioxide production from carbon dioxide Emitting industries, *Separation Science Technology* **44**, 1273-1421.
- El-Azzami L.A., Grulke E.A. (2008) Carbon dioxide separation from hydrogen and nitrogen by fixed facilitated transport in swollen chitosan membranes, *Journal Membrane Science* **323**, 2, 225-234.
- Favre E. (2007) Carbon dioxide recovery from post combustion processes: Can gas permeation membranes compete with absorption? *Journal Membrane Science* **294**, 50-59.
- Favre E., Bounaceur R., Roizard D. (2009) A hybrid process combining oxygen enriched air combustion and membrane separation for postcombustion carbon dioxide capture, *Separation Purification Technology* **68**, 30-36.
- Figuroa J.D., Fout T., Plasynski S., McIlvried H., Srivastava R.D. (2008) Advances in CO₂ capture technology — The U.S. Department of Energy's Carbon Sequestration Program, *International Journal of Greenhouse Gas Control* **2**, 1, 9-20.
- Francisco G.J., Chakma A., Feng X. (2010) Separation of carbon dioxide from nitrogen using diethanolamine-impregnated poly(vinyl alcohol) membranes, *Separation Purification Technology* **71**, 2, 205-213.
- Franz J., Schiebahn S., Zhao L., Riensche E., Scherer V., Stolten D. (2013) Investigating the influence of sweep gas on CO₂/N₂ membranes for post-combustion capture, *International Journal Greenhouse Gas Control* **13**, 180-190.

- Freeman B. (1999) Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes, *Macromolecules* **32**, 375-380.
- Hagg M.B., Sandru M., Kim T.J., Capala W., Huijbers M. (2012) Report on pilot scale testing and further development of a facilitated transport membrane for CO₂ capture from power plants, *Euromembrane 2012*, London, UK, 23-27 Sept.
- Hendriks C., Visser E., Jansen D., Carbo M., Ruijg G.J., Davison J. (2009) Capture of CO₂ from medium-scale emission sources, *Energy Procedia* **1**, 1, 1497-1504.
- Herzog H. (1991) Feasibility, modeling and economics of sequestering power plant CO₂ emissions in the deep ocean, *Environmental Progress* **10**, 64-74.
- Herzog H. (2001) What future for carbon capture and sequestration? *Environmental Science Technology* **35**, 148A-153A.
- Ho M.T., Allinson G., Wiley D.E. (2006) Comparison of CO₂ separation options for geo-sequestration: are membranes competitive? *Desalination* **192**, 1-3, 288-295.
- Ho M.T., Allinson G.W., Wiley D.E. (2008) Reducing the cost of CO₂ capture, from flue gases using membrane technology, *Industrial Engineering Chemistry Research* **47**, 1562-1568.
- Huang J., Zou J., Ho W.S.W. (2008) Carbon dioxide capture using a CO₂-selective facilitated transport membrane, *Ind. Eng. Chem. Res.* **47**, 1261-1267.
- Hughes R., Jiang B. (1995) The permeabilities of carbon dioxide, nitrous oxide and oxygen and their mixtures through silicone rubber and cellulose acetate membranes, *Gas Separation Purification* **9**, 27-30.
- Jeon J.K., Ihm S.K., Park Y.K., Kim J.S., Dong J.I., Kim S., Kim J.M., Kim S., Yoo K.S. (2004) Membrane/PSA hybrid process for carbon dioxide recovery at low concentration, *Studies Surface Science Catalysis* **153**, 543-546.
- Kaldis S.P., Kapantaidakis G.C., Sakellaropoulos G.P. (2000) Simulation of multicomponent gas separation in a hollow fiber membrane by orthogonal collocation – Hydrogen recovery from refinery gases, *Journal Membrane Science* **173**, 61-71.
- Kim J.H., Lee Y.M. (2001) Gas permeation properties of poly (amide-6-b-ethylene oxide)-silica hybrid membranes, *Journal Membrane Science* **193**, 2, 209-225.
- Kim T.-J., Vralstad H., Sandru M., Hagg M.-B. (2013) Separation performance of PVAm composite membrane for CO₂ capture at various pH levels, *Journal Membrane Science* **428**, 218-224.
- Koros W. (1993) Membrane-based gas separation, *Journal Membrane Science* **83**, 1-80.
- Kotowicz J., Bartela L. (2012) Optimisation of the connection of membrane CCS installation with a supercritical coal-fired power plant, *Energy* **38**, 1, 118-127.
- Krishna R., van Baten J.M. (2011) Investigating the potential of MgMOF-74 membranes for CO₂ capture, *Journal Membrane Science* **377**, 1-2, 249-260.
- Krishna R., van Baten J.M. (2012) A comparison of the CO₂ capture characteristics of zeolites and metal-organic frameworks, *Separation Purification Technology* **87**, 5, 120-126.
- Lie J.A., Vassbotn T., Hagg M.B., Grainger D., Kim T.J., Mejdell T. (2007) Optimization of a membrane process for CO₂ capture in the steelmaking industry, *International Journal Greenhouse Gas Control* **1**, 309-317.
- Liu L., Chakma A., Feng X. (2005) CO₂/N₂ separation by poly (Ether Block Amide) Thin Film Hollow fiber composite membranes, *Ind. Eng. Chem. Res.* **44**, 6874-6882.
- Low B.T., Zhao L., Merkel T.C., Weber M., Stolten D. (2013) A parametric study of the impact of membrane materials and process operating conditions on carbon capture from humidified flue gas, *Journal Membrane Science* **431**, 139-155.
- Luis P., Van Gerven T., Van der Bruggen B. (2012) Recent developments in membrane-based technologies for CO₂ capture, *Progress Energy Combustion Science* **38**, 3, 419-448.
- Lynghjem A., Jakobsen J., Kobro H., Lund A., Gjerset M. (2004) The Combicap cycle-efficient combined cycle power plant with CO₂ capture, *2nd Trondheim Conference on CO₂ Capture*, Trondheim, Norway, 24-25 Oct.
- Matson S. (1983) Separation of gases with synthetic membranes, *Chemical Engineering Science* **38**, 503-524.
- Matsumiya N., Teramoto M., Kitada S., Matsuyama H. (2005) Evaluation of energy consumption for separation of CO₂ in flue gas by hollow fiber facilitated transport membrane module with permeation of amine solution, *Separation Purification Technology* **46**, 26-32.
- Matsuyama H., Terada A., Nakagawara T., Kitamura Y., Teramoto M. (1999) Facilitated transport of CO₂ through polyethylenimine/poly(vinyl alcohol) blend membrane, *J. Membrane Sci.* **163**, 221-227.
- Merkel T., Lin H., Wei X., Baker R. (2010) Power plant post-combustion carbon dioxide capture: An opportunity for membranes, *Journal Membrane Science* **359**, 1-2, 126-139.
- Metz S.J., Mulder M.H.V., Wessling M. (2004) Gas permeation properties of poly(ethylene oxide) poly(butylene terephthalate) block copolymers, *Macromolecules* **37**, 4590-4597.
- Petzold L.R. (1983) A description of DASSL: A differential/algebraic system solver, in *Scientific Computing*, Stepleman R.S. et al. (eds), North-Holland, Amsterdam.
- Ramasubramanian K., Winston Ho W.S. (2011) Recent developments on membranes for post-combustion carbon capture, *Current Opinion Chemical Engineering* **1**, 1, 47-54.
- Robeson Lloyd M. (2008) The upper bound revisited, *Journal Membrane Science* **320**, 1-2, 390-400.
- Sandru M., Haukebø S.H., Hägg M.-B. (2010) Composite hollow fiber membranes for CO₂ capture, *Journal Membrane Science* **346**, 1, 172-186.
- Sandru M., Kim T.-J., Capala W., Huijbers M., Hagg M.-B. (2012) Pilot scale testing of polymeric membranes for CO₂ capture from coal fired power plants, *GHGT11*, Kyoto, Japan, Nov.
- Scholes C.A., Stevens G.W., Kentish S.E. (2010) The effect of hydrogen sulfide, carbon monoxide and water on the performance of a PDMS membrane in carbon dioxide/nitrogen separation, *Journal Membrane Science* **350**, 189-199.
- Sheinbaum C., Ozawa L. (1998) Energy use and CO₂ emissions for cement industry, *Energy* **23**, 725-732.
- Skorek-Osikowska A., Kotowicz J., Janusz-Szymanska K. (2013) Comparison of the energy intensity of selected CO₂ capture methods applied to ultra-supercritical coal power plants, *Energy Fuels*, doi:10.1021/ef201687d.
- Steenveeldt R., Berger B., Torp T.A. (2006) CO₂ capture and storage: closing the knowing doing gap, *Chemical Engineering Research Development* **84-A9**, 739-763.

- Van der Sluijs J.P., Hendriks C.A., Block K. (1992) Feasibility of polymer membranes for carbon dioxide recovery from flue gases, *Energy Conversion Management* 33429-33436.
- White J.C., Dutta P.K., Shqau K., Verweij H. (2010) Synthesis of ultrathin zeolite Y membranes and their application for separation of carbon dioxide and nitrogen gases, *Langmuir* 26, 10287-10293.
- Xomeritakis G., Tsai C.Y., Brinker C.J. (2005) Microporous sol-gel derived aluminosilicate membrane for enhanced carbon dioxide separation, *Separation Purification Technology* 42, 249-257.
- Xomeritakis G., Liu N.G., Chen Z., Jiang Y.-B., Köhn R., Johnson P.E., Tsai C.-Y., Shah P.B., Khalil S., Singh S., Brinker C.J. (2007) Anodic alumina supported dual-layer microporous silica membranes, *Journal Membrane Science* 287, 2, 157-161.
- Yave W., Szymczyk A., Yave N., Roslaniec Z. (2010a) Design, synthesis, characterization and optimization of PTT-b-PEO copolymers: A new membrane material for CO₂ separation, *Journal Membrane Science* 362, 1-2, 407-416.
- Yave W., Car A., Peinemann K.V. (2010b) Nanostructured membrane material designed for carbon dioxide separation, *Journal Membrane Science* 350, 124-129.
- Zanderighi L. (1996) Evaluation of the performance of multi-stage membrane separation cascades, *Separation Science Technology* 31, 1291-1308.
- Zha H., Rubin E.S. (2013) Techno-economic assessment of polymer membrane systems for postcombustion carbon capture at coal-fired power plants, *Environmental Science Technology* 47, 6, 3006-3014.
- Zhang Y.-T., Zhang L., Chen H.-L., Zhang H.-M. (2010) Selective separation of low concentration CO₂ using hydrogel immobilized CA enzyme based hollow fiber membrane reactors, *Chemical Engineering Science* 65, 10, 3199-3207.
- Zhao L., Riensche E., Menzer R., Blum L., Stolten D. (2008) A parametric study of CO₂/N₂ gas separation membrane processes for post-combustion capture, *Journal Membrane Science* 325, 284-294.
- Zhao L., Menzer R., Riensche E., Blum L., Stolten D. (2010) Multi-stage gas separation membrane processes with post-combustion capture: energetic and economic analyses, *Journal Membrane Science* 359, 160-172.
- Zolandz R., Fleming G.K. (1995) Gas permeation applications, in *Membrane Handbook*, Ho W.S., Sirkar K.K. (eds), Van Nostrand Reinhold, New York.

Manuscript accepted in June 2013
Published online in December 2013

Copyright © 2013 IFP Energies nouvelles

Permission to make digital or hard copies of part or all of this work for personal or classroom use is granted without fee provided that copies are not made or distributed for profit or commercial advantage and that copies bear this notice and the full citation on the first page. Copyrights for components of this work owned by others than IFP Energies nouvelles must be honored. Abstracting with credit is permitted. To copy otherwise, to republish, to post on servers, or to redistribute to lists, requires prior specific permission and/or a fee: Request permission from Information Mission, IFP Energies nouvelles, fax. +33 1 47 52 70 96, or revueogst@ifpen.fr.