

Review

Membrane-based carbon capture from flue gas: a review

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ABSTRACT

There has been an increasing interest in the application of membranes to flue gas separation, primarily driven by the need of carbon capture for significantly reducing greenhouse gas emissions. Historically, there has not been general consensus about the advantage of membranes against other methods such as liquid solvents for carbon capture. However, recent research indicates that advances in materials and process designs could significantly improve the separation performance of membrane capture systems, which make membrane technology competitive with other technologies for carbon capture. This paper mainly reviews membrane separation for the application to post-combustion CO₂ capture with a focus on the developments and breakthroughs in membrane material design, process engineering, and engineering economics.

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1. Introduction

In the United Nation's Earth Summit held June 1992 in Brazil, a treaty known as Nations Framework Convention on Climate Change (UN-FCCC) was made in order to stabilize greenhouse gas concentrations in the atmosphere. This treaty came into force gradually as more countries signed it, which accelerated research and development on different carbon dioxide (CO₂) capture technologies. Since that time, a few technologies have been developed for post-combustion carbon capture (PCC), including liquid solvent absorption, membranes, solid-sorbent adsorption (Krishnamurthy et al., 2014), membranes (Ho et al., 2008b), and mineralization (Zevenhoven and Fagerlund, 2009).

The first commercial interest in the separation of CO₂ from flue gas was its application for enhanced oil recovery (EOR) (Herzog et al., 1997). Application of CO₂ for EOR started in the 1970s and has proved to be an effective economic approach over the years (Long et al., 2006). When the amount of CO₂ product from natural gas purification is insufficient, the CO₂ from flue gases emitted from nearby power plants can be utilized using various carbon capture technologies for the EOR application. Currently, amine-based carbon capture technologies (shown Fig. 1), such as Flour Econamine Plus, are commercially available for implementation (Aaron and

Tsouris, 2005; Desideri and Paolucci, 1999; Rao and Rubin, 2002), while other technologies, including membranes, lie at different developmental stages from concept to pilot-scale testing. Solvent-based PCC, in spite of being the best available technology (BAT) for dealing with various flue gas streams given in Table 1, may not be a long-term desired technology for PCC due to its high energy penalty associated with solvent regeneration (Feron, 2009). Different from solvent technologies for post-combustion CO₂ capture, membrane technology is a physical separation process shown in Fig. 2 where gas mixtures consisting of two or more components are separated by a semipermeable barrier into a retentate stream and a permeate stream. The main advantages of membrane separation against other technologies include compactness, modularity, ease of installation by skid-mounting, ability to be applied in remote areas (such as offshore), flexibility in operation and maintenance, and, in most cases, lower capital cost as well as lower energy consumption (Seader and Henley, 2006). They also require very little chemicals compared to conventional separation processes (He and Hägg, 2012).

Aaron and Tsouris (2005) reviewed various methods for CO₂ removal from flue gas including solvent absorption, pressure- and temperature-swing adsorption using various solid sorbents, cryogenic distillation, and membranes. They concluded that the most promising method for CO₂ separation is liquid absorption using monoethanolamine (MEA); however, the development of ceramic and metallic membranes for membrane diffusion will produce membranes that are significantly more efficient at separation than

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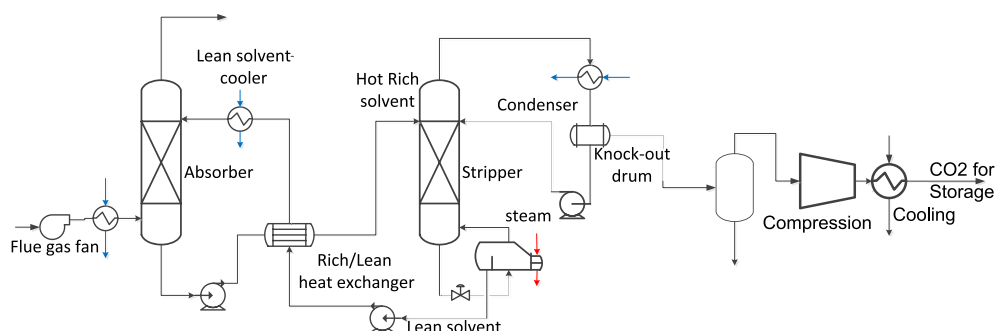


Fig. 1. Typical solvent-based process for carbon capture from flue gas streams.

Table 1

Typical conditions of a flue gas stream from various sources (Metz et al., 2005).

Stream sources	CO ₂ concentration %vol (dry)	Pressure range	CO ₂ partial pressure (bar)
Gas turbines	3–4	Atmospheric	0.03–0.04
Fired boilers of oil refinery and petrochemical plant	8	"	0.08
Natural gas fired boiler	7–10	"	0.07–0.10
Oil fired boilers	11–13	"	0.11–0.13
Coal fired boilers	12–14	"	0.12–0.14
IGCC after combustion	12–14	"	0.12–0.14
Blast furnace (after combustion)	27	"	0.27
Cement process	14–33	"	0.14–0.33

the liquid absorption method. The special report by the Intergovernmental Panel on Climate Change (IPCC) (Metz et al., 2005) mentioned that membranes for flue gas separation had not yet been trialed in large scale systems, and their reliability and costs were not fully evaluated at that time. But the report was optimistic about the future of this application via worldwide R&D efforts that aimed at the manufacturing of more suitable membrane materials for CO₂ capture in large-scale applications.

Membranes for carbon dioxide separation have been applied to natural gas sweetening where the concentrations of CO₂ and H₂S contained in high-pressure natural gas should be lowered to the levels of meeting the gas pipeline specifications (CO₂ < 2% and H₂S < 4 ppm) (Baker and Lokhandwala, 2008; Ettouneya et al., 1995; Peters et al., 2011). Numerous commercial membrane technologies have been available for natural gas sweetening. However, this does not necessarily ensure the feasibility of membranes for flue gas treatment because of several key differences between the two applications: (1) Membranes are good for bulk separation, but generally are not an economical option for cases with either a low feed concentration or a high-purity product requirement. Thus, membranes are used for natural gas sweetening only when the CO₂ concentration of a well gas stream is sufficiently high. Otherwise, a

hybrid system combining membranes with an absorption process is used to separate the bulk of CO₂ via membrane and the remainder, down to pipeline specification, with absorption system; (2) Unlike well gas streams with high pressures, flue gas streams are typically at atmospheric pressure and require either costly compression or vacuum pumping to generate driving force for membrane gas separation; and (3) Different molecular characteristics of CH₄/CO₂ separation and CO₂/N₂ separation involve in membrane gas separation processes.

Membrane research and development for CO₂ capture could be divided into two categories: membrane material design (MMD) and membrane systems engineering (MSE). The fundamental goal of MMD is to synthesize membranes of desirable permeance and selectivity while having chemically and physically stable structures. On the other hand, the major goal of MSE is to develop membrane capture processes with optimal configurations to achieve the separation targets (e.g., CO₂ removal rate and product purity) at minimum capital and operational expenditures (CAPEX and OPEX).

This paper mainly reviews membrane separation for the application to post-combustion CO₂ capture with a focus on the developments and breakthroughs in membrane material design, process engineering, and process economics. In the following sections, we first review and analyze the studies on MMD for PCC applications. This is followed by an MSE literature survey. The next focus is on the techno-economics of MPCC in comparison with other capture technologies. Last, we discuss the limitations of current MPCC research and potential improvement opportunities.

2. Membrane material design (MMD)

2.1. Non-facilitated membranes

Non-facilitated membranes rely on the “solution-diffusion” transport process whereby the permeate first dissolves into the membrane and then diffuses through it. The solubility of the permeate follows the Henry’s law. For a given temperature, the

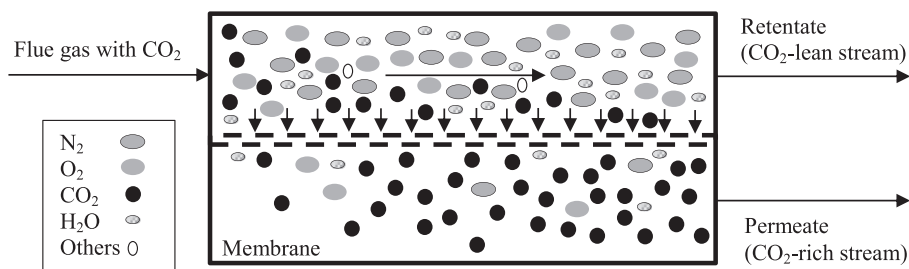


Fig. 2. Schematic of membrane-based CO₂ separation process from flue gas streams.

amount of a gas dissolved per unit volume is proportional to the partial pressure of the gas in equilibrium with it, described as Eq. (1):

$$C_i = P_i/K_{Hi} = P_iK_i \quad (1)$$

where C_i is the dissolved concentration, P_i is the partial pressure, K_{Hi} the Henry's Law constant, and K_i is the solubility of component i .

Diffusion is governed by Fick's first law of diffusion as presented in Eq. (2):

$$J_i = D_i\Delta C_i/L \quad (2)$$

where J_i is the flux per unit area, D_i is the diffusion co-efficient in the membrane, and ΔC_i is the difference in concentration across the membrane width, L .

Substituting Eq. (1) into Eq. (2) gives:

$$J_i = K_iD_i\Delta P_i/L \quad (3)$$

where ΔP_i is the difference in partial pressure across the membrane. The membrane selectivity is dependent upon the relative rates of these processes.

$$\alpha_{i/j} = J_i/J_j \quad (4)$$

A schematic representation of this mechanism is presented in Fig. 3.

The major advantage of non-facilitated membranes is that there is a high tunable degree of controlling the membrane permeability and selectivity via the manipulation of polymer preparation and chemical composition. Counteracting this is the characteristic swelling and plasticization of the materials as a result of CO_2 absorptions. Additionally, this material is generally only suitable for low temperature applications.

The pioneering work on CO_2/N_2 separation using non-facilitated membranes may be traced back to the study by Kawakami et al. (1982) who blended a low permeable glassy polymer (cellulose nitrate) with a plasticizer membrane (polyethylene glycol (PEG)). They noticed that with the increase of PEG percentage and/or molecular weight, the permeability of CO_2 as well as CO_2/N_2 selectivity increased. However, above a threshold concentration (30% PEG) plasticization was observed. The interesting point of this research was that the authors did not have a clear idea on industrial applications for this process and only projected that the separation of CO_2 from N_2 might be used "in order to recover carbon resources or to control CO_2 concentration in an artificial atmosphere."

Sidhoum et al. (1988) studied CO_2/N_2 separation using cellulose acetate (CA) hollow fibers with dense skin on the outside. They

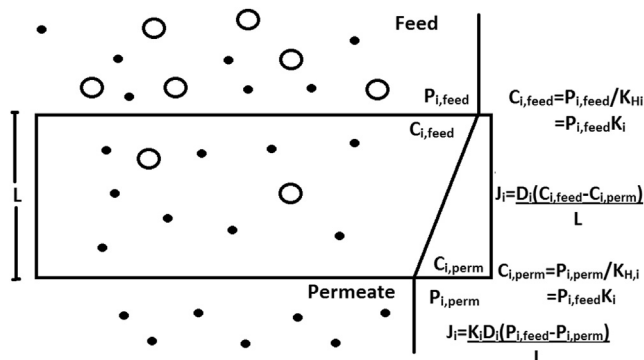


Fig. 3. Non-facilitated transport mechanism.

compared separation efficiency with the high-pressure feed on the outside and the inside of the fibers and reported permeances of about 20, 3, and 0.8 GPU¹ for CO_2 , N_2 , and O_2 , respectively. They also claimed that the inherent membrane separation capability appeared the same whether the feed was inside or outside of the fibers. Sada et al. (1992) examined separation characteristics of $\text{CO}_2/\text{N}_2/\text{O}_2$ mixtures using hollow fiber modules of asymmetric cellulose triacetate membrane with a countercurrent plug flow model. They reported ideal selectivity of CO_2 relative to N_2 in the range of 21–24. Polyethersulfones (PES) have a higher glass-transition temperature than cellulose triacetate, thus making them more resistant to plasticization. Kumazawa et al. (1993) used PES membranes and reported CO_2/N_2 ideal selectivities of 35 and 40 for asymmetric and homogenous membranes respectively.

Cellulose acetate membranes were later discarded due to their problems with plasticization (Bernardo et al., 2009; Scholes et al., 2008) though some studies showed that blending CA with other polymers such as PEG could improve the membrane performance (Li et al., 1995).

Tokuda et al. (1997), with knowledge that Cardo polyimides have high CO_2/N_2 permselectivity, studied the impact of various functional groups on selectivity of Cardo polyimides. They noticed that Cardo polyimide (PI-BT-COOMe), having a CO_2 affinitive methylcarboxyl functional group, shows outstanding CO_2/N_2 selectivity behavior. More specifically, Cardo polyimides which had 3,3',4,4'-Benzophenonetetracarboxylic dianhydride as a monomer (PI-BT) obtained the highest separation with CO_2/N_2 selectivity of 52 at 25 °C. Later, it was reported that a bis(phenyl)fluorene-based Cardo polyimide could result in membranes with notably high permeance of 1000 GPU with good CO_2/N_2 selectivity of 40 (Kazama et al., 2004). Yoshino et al. (2000) studied the effects of hard-segment polymers (namely polyurethanes (PUs), polyamides (PAs), and polyamides (PIs)) on CO_2/N_2 separation properties of poly(ethylene oxide) (PEO). The study showed that compared with PEO-PIs, PEO-PUs and PEO-PA had much smaller CO_2 permeability values and somewhat lower or similar CO_2/N_2 selectivity. This was due to small diffusivity and solubility values for CO_2 as a result of the incomplete phase separation. They also noticed that in worst phase separation conditions, PEO-PIs still had CO_2/N_2 selectivity above 50. They reported the best CO_2/N_2 selectivity value of 58 for a PEO-PI. In a similar study, Bondar et al. (2000) studied properties of poly(ether-b-amide) segmented block copolymers. They noticed that CO_2/N_2 selectivities were greater in polymers with higher concentrations of polar groups. They obtained CO_2/N_2 selectivities as high as 56 with CO_2 permeability of approximately 220 Barrers² at 35 °C.

Kim et al. (2001) used a membrane composed of two polymeric materials: a porous substrate and a filling polymer that fills the pore of the substrate. By using this method, they obtained CO_2/N_2 selectivity of 32.4 which is higher than their non-filling membranes. The results justified their proposal that the high selectivity of the pore-filling membrane is attributed to the high solubility selectivity due to the affinity of CO_2 to PEO segment. Nakagawa et al. (2002) synthesized three copolyimide membranes by the condensation polymerization of alicyclic 2,3,5-tricarboxy cyclopentyl acetic dianhydride (TCDA) with diamino diphenyl ether (DADE) and bis(aminopropyl)polydimethylsiloxane (BAS). They observed CO_2/N_2 selectivity of 60 for TCDA-DADE. Lin and Freeman (2004) studied the impact of pressure and temperature on the solubility, diffusivity, and permeability of various gases including CO_2 and N_2 using PEO. PEO exhibited CO_2 permeability coefficient

¹ 1 GPU = 10^{-6} cm³ (STP)/cm² s cmHg. 1 GPU ~ 3.4×10^{-10} mol/m² s Pa.

² 1 Barrer = 10^{-10} cm³ (STP) cm/(cm² s cmHg).

of 12 Barrers, and CO_2/N_2 pure gas selectivity of 48 at 35 °C. PE under similar conditions showed CO_2 permeability of 13 Barrers with the cost of very low CO_2/N_2 selectivity of 13. Charmette et al. (2004) studied properties of cross-linked membranes prepared from PEO and poly(epichlorohydrin) (PEP) at different composition ratios. At PEO/PEP mixtures with high PEO concentrations such as 93/7 and 96/4, a high CO_2/N_2 selectivity above 62 was observed.

In a thorough study, Powell and Qiao (2006) reviewed available membrane materials for flue gas separation, possible design strategies, synthesis, fabrication, and the role of novel materials. Their survey included a number of different classes of polymers such as polyacetylenes, poly(arylene ether), polyarylates, polycarbonates, poly(ethylene oxides), polyimides, 6FDA-based polyimides, poly(-phenylene oxide)s, and polysulfones as well as carbon and mixed matrix membranes. Their survey, which covered some 190 reports, concluded that copolymers and polymer blends had higher potential for further research – of which two materials were the most interesting. The first types are polyimides that incorporate 6FDA due to their gas transport properties, good physical properties, potential structural variations and ease of membrane formation. The second are the PEO segmented copolymers with polyimides having both high selectivities and a high CO_2 permeability possibly due to high solubility of CO_2 in PEO.

Scholes et al. (2008) reviewed the state-of-the-art development in mixed matrix polymeric membranes, facilitated transport polymeric membranes, and other membrane types, e.g., carbon and inorganic. They showed that the trend of research on polymeric membranes aims at improving their performance by incorporating an additional agent into the polymeric phase that could be another polymer (polymeric blends), particulate matter (mixed matrix membranes), or a carrier molecule (facilitated transport). They predicted that such studies will shift Robeson's bound to the upper right corner of a Permeability/Selectivity plot having moderate selectivities and high permeabilities.

Toy et al. (2012), in a project for U.S. Department of Energy, synthesized a vinylidene fluoride (VDF)-based copolymer membrane (VDF-co-B). They observed that the bulky, high-dipole comonomer B helped to increase gas permeability in the polymer matrix, and its greater polarity enhanced the CO_2 affinity (solubility) of the matrix. They reported 2.5–3 times higher CO_2/N_2 selectivity and six times higher CO_2 permeability than those of the PVDF homopolymer.

Some studies have also addressed metallic membranes for PCC applications. For instance, Carapellucci and Milazzo (2003) evaluated the influence of different operating conditions on the behavior of pre- and post-combustion separation units, based on metallic or polymeric membranes. They reported encouraging results for CO_2 capture with integration of a metallic membrane system into a chemically recuperated gas turbine (CRGT) power plant. There has also been an increasing interest in carbon membranes. Although these membranes have shown potential for CO_2 separation, they require further improvements, specially by reducing fiber wall thickness (He and Hägg, 2011).

2.2. Facilitated transport membranes

Facilitated transport membranes, in addition to exhibiting “solution-diffusion” characteristics, 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 Fig. 4. As shown, the CO_2 is absorbed and reacts to form bicarbonate, the form in which it transverse the membrane. Upon reaching the other side it back reacts to form CO_2 and is then released on the permeate side.

Support liquid membranes (SLMs) were the first facilitated transport membranes developed. These systems consisted of a liquid phase containing a carrier species in the pores of a polymer support. The mobile carriers are able to move freely across the membrane and perform well for CO_2 separation processes. However, these systems are relatively unstable as the carriers can be washed out from the system as they are not bonded to the polymer matrix. SLM design was improved by Leblanc et al. (1980) through the development of ion exchange membranes. Electrostatic forces between ionic carriers and the membrane better held the carriers within the membrane. In recent years, ionic liquids have also been used in these systems. Ionic liquids are favorable as they have high temperature durability and negligible volatility. Another variety of facilitated transport membranes are fixed carriers. Fixed carriers are where the reactive group is bound to the polymer backbone of the membrane material. Rather than being transported through the membrane with the mobile carrier, the species ‘hops’ from one fixed carrier to the next through the membrane. Different to gas absorption membranes, facilitated transport membranes rely on the membrane being saturated to enable the required reaction to occur.

Kasahara et al. (2012) prepared amino acid ionic liquid based facilitated transport membranes with tetrabutylphosphonium amino acid ionic liquids and with glycine, alanine, proline, and serine as the anion. Tetrabutylphosphonium was selected due its superior thermal stability. The proline based membrane showed the highest permeability and best CO_2/N_2 selectivity most likely due to its high higher water holding ability.

Zhao and Ho (2012) developed a fixed-site-carrier facilitated transport membrane incorporating sterically hindered polyamines with cross-linked polyvinylalcohol. The incorporation of amine steric hindrance in a solid phase exhibited significantly improved enhancement of CO_2 permeability and CO_2/H_2 and CO_2/N_2 separation performances at 110 °C and a free pressure of 2 atm. Zhao and Ho prepared a new membrane incorporating moderately hindered poly-N-isopropylallylamine as a fixed site carrier alongside mobile carriers creating a cross-linked polyvinylalcohol–poly(siloxane) network (Zhao and Ho, 2013). This new membrane exhibited high

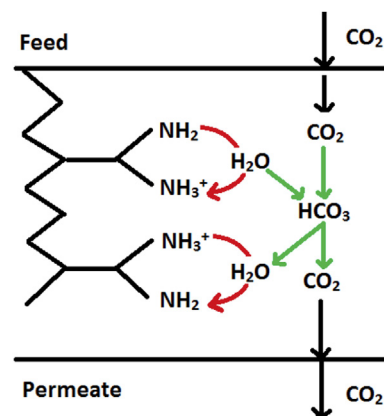


Fig. 4. Schematic of the mechanisms for a fixed carrier amine based facilitated transport membrane.

CO₂ permeability and CO₂/N₂ and CO₂/H₂ selectivity. [Bai and Ho \(2011\)](#) fabricated CO₂ selective facilitated transport membranes based on cross-linked poly(vinyl alcohol) (PVA) and sulfonated polybenzimidazole (SPBI) matrixes with 2-aminoisobutyric acid (IBA-K) and potassium carbonate–bicarbonate as mobile carriers and poly(allylamine) (PAA) or 2-bromobutane functionalized PAA (PAA-C₄H₉) as fixed carriers for CO₂ transport. The cross-linked PVA based membranes showed the best separation performance, likely due to its great hydrophilicity.

[Deng et al. \(2009\)](#) developed an ultra-thin PVAm/PVA blend facilitated transport membrane cast on a porous polysulfone (PSf) support for CO₂–N₂ separation. A separation factor of up to 174 and a CO₂ permeance up to 0.58 m³ (STP)/(m² h bar) were documented. The fixed amino groups in the PVAm matrix function as CO₂ carriers to facilitate the transport whereas the PVA adds mechanical strength.

2.3. Mixed matrix membranes

Mixed-matrix membranes (MMMs), filled with inorganic particles, provide a means to improve the gas separation performance of polymeric membranes. The key challenge with this type of membrane is to ensure that the inorganic particles are well bonded with the polymer thus preventing voids that may result in a loss of selectivity. [Pera-Titus \(2014\)](#) presented a review of inorganic materials that may be suitable for use in polymer membranes for CO₂ capture. Inorganic fillers trialed have included zeolites ([Bastani et al., 2013](#); [Junaidi et al., 2014](#); [Nik et al., 2011](#); [Sublet et al., 2012](#)), carbon nanotubes ([Ahmad et al., 2014](#); [Aroon et al., 2013](#); [Rajabi et al., 2013](#)), and metal organic frameworks (MOFs) ([Nafisi and Hagg, 2014](#); [Perez et al., 2009](#)). The inorganic fillers have been found to improve both the permeability and selectivity of membranes over the base polymer and also effectively restrict the mobility of polymer chains at high CO₂ partial pressures, thus suppressing CO₂ induced plasticization ([Shahid and Nijmeijer, 2014](#)).

[Jiang \(2012\)](#) has provided a comprehensive review on MOF membranes and their application for carbon capture. According to the author, unlike MOF sorbents, very little work has been carried out on MOF membranes and they are still at their infancy, though at very progressive stage. Even amongst the studies on the application of MOF membranes for carbon capture, there has been little attention paid to CO₂/N₂ separation ([Krishna and van Baten, 2011](#)). Therefore, given the very high costs of MOFs synthesis and their lab-scale research status, they may not find a place amongst the potential commercial membranes for MPCC in the medium term.

2.4. Gas membrane contactors

Gas membrane contactors make use of membranes to provide an interface between the gas and liquid as opposed to the using column arrangements, i.e., packed beds, spray towers, etc.

[Feron et al. \(1992\)](#) proposed using gas absorption membranes, with solvents such as MEA on the permeate side. They reported that such configuration was more promising as it combines the advantages of absorption technology (high selectivity) and membrane technology (compactness of equipment). These types of equipment are now generally referred to as membrane gas contactors (MGC). The major advantage of these systems over traditional packed bed based solvent systems is the elimination of the need for phase dispersion. In membrane contactors, the mass transfer interface is set in the membrane pores, where the pore volume is occupied by one of the two phases.

The most common and widely reported negative characteristic of MGC systems is the additional resistance to mass transfer that

the membrane provides. However, when the system is operated in the “non-wetted” mode, i.e., pores filled with gas, not solvent, the resistance is several orders of magnitude smaller than that of the liquid film resistance which results in a negligible overall effect on the overall mass transfer coefficient. A schematic is presented in [Fig. 5](#).

Prediction of whether an MGC system will operate in the “wetted” or “non-wetted” mode is primarily controlled by the parameters of the Young–Laplace equation ($\Delta P_c = -4\lambda \cos \theta/d$). ΔP_c is the critical breakthrough pressure, i.e., the differential pressure at which pores will become “wetted,” λ is the surface tension of the solvent, θ is the contact angle in degrees for the gas–solvent–membrane system, and d is the effective diameter of the membrane pore (assuming that the pores are circular in shape).

The membranes themselves are unlike gas separation membranes as they exhibit no intrinsic selectivity; rather, selectivity of the system is provided by the solvent used. In CO₂ capture systems the most common solvents used are alkanolamines (i.e., monoethanolamine (MEA), Diethanolamine (DEA), etc.) due to their high CO₂ loading capacities, high absorption rates, and low regeneration rates. However, alkanolamines also have low surface tensions, and so investigation into performance of other solvents is warranted.

As high solvent to membrane contact angles are favorable, membranes are typically synthesized from hydrophobic materials such as polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE), poly(tetrafluoroethylene-co-perfluorovinylether) (PFA), and polyvinylidene fluoride (PVDF). A wide variety of investigations involving these membranes in association with alternate solvents are presented in [Table 2](#). PP membranes are commercially available and inexpensive, and therefore are most commonly used; however, they generally exhibit a poorer performance. PP is not as hydrophobic as the fluorine containing polymeric membranes (PTFE and PVDF) and so are more susceptible to “pore wetting” inhibiting performance.

[Yeon et al. \(2003\)](#) investigated the mass transfer behavior of carbon dioxide through a membrane contactor system comprising PTFE and PVDF hollow fiber membranes with MEA. They found that the PVDF was more resistant to “pore wetting” and so exhibited superior carbon dioxide mass transfer performance. As suggested by the investigations presented in [Table 2](#), the base membranes used for membrane contactors have been well characterized. Current work is focused on modifications of these materials to improve performance.

A number of methods based on the modification of the base membrane materials are being investigated to improve the performance of gas absorption membranes. These include: plasma

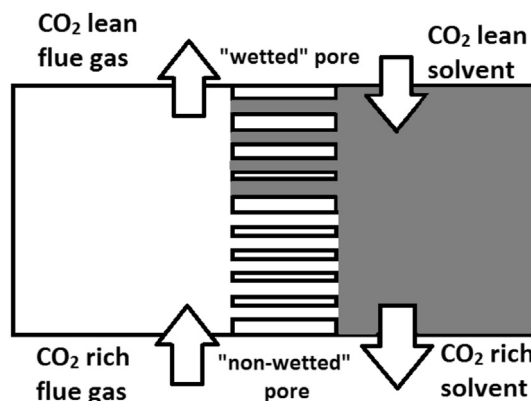


Fig. 5. Gas–liquid membrane contactor for CO₂ removal from flue gas showing “wetted” and “non-wetted” pores.

Table 2
Gas absorption membranes.

Traditional membrane material				
Membrane material (abbreviation)	Reference	Gases separated	Solvent(s) trialed	Comments
Polypropylene (PP)	(Wang et al., 2013)	N ₂ /CO ₂	MEA, DEA, MDEA, MEA/MDEA, DEA/2-amino-2-methyl-1-propanol (AMP), and MDEA/PZ	Pore wetting observed with MEA, but not potassium carbonate
	(Scholes et al., 2012)	CO ₂ , CO, H ₂ , N ₂ , CH ₄	Monoethanolamine, potassium carbonate	
	(Ozturk and Hughes, 2012)		Water, 10 wt% MEA, 10 wt% DEA	Rate controlled by absorbent flow rate
	(Khaisri et al., 2009)	CO ₂	MEA	
	(Zhang et al., 2008)	N ₂ /CO ₂	Water	
	(Bottino et al., 2008)	N ₂ /CO ₂	Monoethanolamine (MEA), [3 M]	
	(Zhang et al., 2008)	N ₂ /CO ₂	Diethanolamine (DEA) [2 M]	
	(Yan et al., 2007)	N ₂ /CO ₂ /O ₂	Potassium Glycinate (PG)	
(Yan et al., 2007)	N ₂ /CO ₂ /O ₂	Monoethanolamine (MEA) [0.5–3 M]	Limited wetting observed	
(Yan et al., 2007)	N ₂ /CO ₂ /O ₂	Methyldiethanolamine (MDEA) [0.5–3 M]		
Polyvinylidene fluoride (PVDF)	(Zhang et al., 2008)	N ₂ /CO ₂	Water	Rate controlled by absorbent flow rate
	(Zhang et al., 2008)	N ₂ /CO ₂	Diethanolamine (DEA) [2 M]	Membrane wetting
	(Mansourizadeh and Ismail, 2009)	N ₂ /CO ₂	Diethanolamine (DEA)	
	(Yeon et al., 2003)	25% CO ₂ , 75% N ₂	Monoethanolamine, MEA, 5 wt%	
Polytetrafluoroethylene (PTFE)	(Scholes et al., 2012)	CO ₂ , CO, H ₂ , N ₂ , CH ₄	Monoethanolamine [30 wt%], potassium carbonate [30 wt%]	Pore wetting observed with MEA, but not potassium carbonate
	(Yeon et al., 2003)	25% CO ₂ , 75% N ₂	Monoethanolamine, MEA, 5 wt%	
	(Kim and Yang, 2000)	CO ₂ , N ₂	2-Amino-2-methyl-1-propanol (AMP)	

treatment, applying a thin hydrophobic layer to base membrane materials, incorporation of salts into the membranes during manufacture, and changing manufacturing parameters to alter membrane characteristics such as pore diameter.

Bae et al. (2001) compared the performance of Freon-116, allylamine, water, and acrylic acid for gas plasma treatment of polypropylene membranes. They found that the oxygen containing chemical species, i.e., water and acrylic acid, deteriorates the membrane pores and allylamine grafted to the surface thereby reducing the membrane effectiveness. Freon-116 gas treatment made no change to the surface morphology and no deterioration of the pores was observed, yet fluoro-carbon molecules were grafted to the surface. Additionally, only Freon-116 resulted in an increase in solvent membrane contact angle while the others were reduced.

Lin et al. (2009b) examined plasma treated PP membranes and reported significant improvements including: an increase in the water contact angle of the membrane from 117° to 143°, increased durability, an 8% increase in the CO₂ absorption flux when using 1.0 mol/dm³ AMP as the absorbent, and a decrease in the wetting ratio with mixed AMP–PZ absorbent from 0.0674% to 0.027%.

Franco et al. (2012) undertook polytetrafluoroethylene (PTFE) plasma sputtering of polypropylene (PP) membranes. This process resulted in the formation of an ultrathin fluorinated hydrophobic surface that retained the microporous surface of the PP membrane. The novel material outperformed the unamended PP membrane for CO₂ mass transfer rate with MEA solvent flowing through the fiber lumen by approximately 30%. Upon exposure to MEA, the plasma treated membranes were found less susceptible to degradation and wetting as compared to the untreated material. Lin et al. (2009a) plasma treated (CH₄) PVDF and used an aqueous mixture of alkanolamines (PZ, MEDA and AMP) as absorbents. The water, AMP and AMP + PZ mixture contact angles ranged 145–155° for the modified PVDF, whilst PVDF and PTFE ranged 132–136° with the contact angle sequence mirrored for CO₂ absorption rates. Another study reported that PVDF/siloxane nanofibrous membranes, compared with PVDF, exhibit higher solvent resistance and mechanical strength (Lin et al., 2014b). These properties make them better alternatives for carbon capture applications.

Ahmad et al. (2013) deposited a superhydrophobic layer of low-density polyethylene (LDPE) onto poly(vinylidene fluoride) (PVDF). The material developed was porous with a 152° ± 3.2 water contact angle and maintained a higher CO₂ flux than the unamended PVDF membrane. Mosadegh-Sedghi et al. (2013) developed highly hydrophobic microporous low density polyethylene membranes through incorporation of sodium chloride particles into the structure. This treatment resulted in an increase of the water contact angle from 98° to 130°.

Ghasem et al. (2012) investigated extrusion temperature effects (from 150 to 170 °C) on the pore size, water contact angle, strength, and porosity for poly(vinylidene fluoride) (PVDF) hollow fiber membranes. With increased temperatures the pore radius decreased and the porosity and water contact angle increased, resulting in improved CO₂ fluxes across the membrane.

Rajabzadeh et al. (2013) fabricated PVDF hollow fiber membranes with different membrane porosities on the inner surface. They then applied the membranes for CO₂ absorption using two concentrations of MEA: 2 M and 4 M. No difference in CO₂ absorption rates was observed for any membrane porosity when used in associated with a 2 M MEA solvent, while the capture rate for the larger porosity membrane increased when 4 M MEA was used. The long-term studies reported wetting for all materials when used with 4 M MEA, but only for the larger porosity membranes for the 2 M concentration. Lin et al. (2013) coated highly porous SiO₂ aerogels, modified with hydrophobic fluorocarbon functional groups (–CF₃), onto a macroporous Al₂O₃ membrane. This hydrophobic coating enabled long-term continuous CO₂ capture with large absorption flux enhancements. The authors also examined the use of methyltrimethoxysilane (MTMS) precursors for coating. The MTMS-derived hydrophobic membrane exhibited CO₂ absorption with fluxes at least 500% higher than the uncoated MTMS-based aerogel membranes (Lin et al., 2014a).

2.5. Discussion on membrane material design

Seader and Henley (2006) 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. Suitable membranes for carbon capture should have all these attributes. However, most of the existing studies on CO₂ capture membranes are focused on improving selectivity and lack sufficient attention to other important requirements. Furthermore, the impacts of other flue gas components, such as water vapor, O₂, SO_x, NO_x, NH₃, etc., have been ignored widely in literature. With a few exceptions (Hussain and Hägg, 2010; Merkel et al., 2010; Reijerkerk et al., 2011; Sada et al., 1992; Scholes et al., 2010), the existing studies mainly focus on a binary mixture of N₂ and CO₂ and most of the available selectivity values are reported only for this binary mixture.

The existing experimental studies mainly analyze the permeability of pure gases and then estimate the CO₂/N₂ selectivity. However, permeability of a gas at pure versus mixture conditions may vary remarkably due to different molecules' competition in diffusion and sorption (Koros and Fleming, 1993). Understanding the important role of minor components in the design and operation of membranes for carbon capture, Scholes et al. (2009) reviewed those polymeric membranes considering the impacts of minor gases on membrane permeability, plasticization, and aging effects. They concluded that “while many minor components can affect performance both through competitive sorption and plasticization, much remains unknown. This limits the selection process for membranes in this application.” One good example for illustration is regarding the effect of water vapor. There has been traditional thought that water, due to its higher permeability than CO₂ plus solubility of CO₂ in water, will cause a plasticization effect. It will moreover result in part of the CO₂ to be lost due to dissolution in water. However, Merkel et al. (2010) found that the presence of water has a beneficial effect of providing an internal sweep due to diluting the permeate and thus increasing the CO₂ permeation driving force through the membrane. The water content of permeate could be removed through the intercoolers of the multistage compression of CO₂ before transport to a storage site. Similar results on the positive impact of water have been reported for PVAm facilitated transport membranes (Hussain and Hägg, 2010) and poly(ethylene oxide) based block copolymers (Reijerkerk et al., 2011). In a contradicting study, Scholes et al. (2010) associated water with negative impacts. The work of Scholes et al. (2010) involved the experimental determination of the effect of minor gas components such as carbon monoxide, hydrogen sulfide, and water on the performance of a polydimethyl siloxane (PDMS) rubbery membrane in CO₂/N₂ separation. Examining the syngas of integrated gasification combined cycle processes, Scholes et al. (2010) showed that the permeability of both CO₂ and N₂ over PDMS decreased with the addition of these components due to competitive sorption of these gases, with the exception of positive impact of H₂S on N₂ permeability. The negative effect of water vapor on the permeability of N₂ and CO₂ is due to the hydrophobic nature of PDMS resulting in very low water sorption. Using the Flory–Huggins theory, they justified that water occupies the free volume within PDMS and then results in lower CO₂ and N₂ permeability. Low et al. (2013) have also highlighted that though water vapor in flue gas can have a slight positive sweep effect on process performance, its effect on membranes can be complex depending on possible interactions of sorbed water with the membrane. An interesting discussion also is provided by Jiang (2012) on the notably complex impact of water on CO₂ capture over MOFs. For instance, water impact can be positive on CO₂ separation at a certain pressure range and negative at another pressure range. Future studies, therefore, may need to measure the permeability and selectivity of CO₂/N₂ under the mixture condition,

or even under the condition of real flue gas compositions, while considering oxygen and water vapor at least.

Therefore, it can be concluded that research in the field of membrane material design (MMD) is more complex and has a wider spectrum than just focusing on improving the permselectivity of CO₂/N₂ over a narrow operating condition. Other membrane attributes, i.e., stability and compatibility, while considerations of the real process environment and operational parameters are yet to be well explored. Commercialization of membranes might not be possible without addressing these critical technical and operational concerns in various scales from lab to pilot plant.

3. Process systems design for membrane-based carbon capture (MPCC)

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). Modeling and optimization are essential in MSE work which are nowadays more facilitated by faster computers and enhanced algorithms. Membranes require high pressures in order to generate driving force and facilitate mass transfer. With notable increase in energy prices within the last decade, the importance of optimal system design has remarkably increased in order to minimize the operational costs and thus enhance the overall performance of membranes, especially in the conditions that there are competing alternatives for membranes.

Bernardo et al. (2009) 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.” Similar conclusions are reported elsewhere (He et al., 2013). Here, we review membrane processes in unit and network levels and discuss the complementary nature of MMD and MSE.

3.1. Membrane unit modeling

There have been numerous efforts in membrane modeling over the last six decades. Weller and Steiner (1950a,b) first proposed a method to calculate the permeate composition of a binary gas mixture in a cross-flow process while assuming negligible pressure drop. Brubaker and Kammermeyer (1954) were the first to tackle the topic of multicomponent membrane separation. They introduced a method to solve a perfect-mixed membrane. However, the model was limited to three or four components, exposing the complex nature of membrane modeling. Stern et al. (1965) presented a general algorithm for multicomponent gas mixtures. It was a trial and error method in perfect-mixing flow condition.

Though there were other efforts (Pan and Habgood, 1978a, b; Sengupta and Sirkar, 1984) that tackled this problem, it was Shindo et al. (1985) who presented a complete calculation method for multicomponent gas mixtures at five different flow patterns (one-side-mixing, perfect-mixing, cross flow, countercurrent, and cocurrent). The study was based on flat membranes with the assumption of negligible pressure drop on both sides of the membrane. It concluded that countercurrent flow could result in higher permeate purity. A similar study was carried out by Li et al. (1990) reporting the outperformance of countercurrent flow. Recently, Alshehri et al. (2013) improved the Shindo et al. (1985) model by adding Hagen–Poiseuille approximation formula for describing the permeate pressure change in the fiber lumen.

Pan (1986), expanding on his previous models (Pan, 1983; Pan and Habgood, 1974, 1978a, b), presented a model of

multicomponent permeation with high-flux, asymmetric hollow-fiber membranes. The model considered the permeate pressure variation inside the fiber. A thorough review of efforts done for gas membrane modeling till 1992 could be found in Kovvali et al. (1992).

In a different type of modeling, Coker et al. (1998) introduced an algebraic stage-wise method by dividing the length of hollow fiber into a series of S stages in the axial direction and mass balances were enforced in each section. They developed a model for cocurrent, countercurrent, and cross flow contacting patterns considering permeate sweep, pressure-dependent permeability coefficients, and bore side pressure gradients. The existence of a boundary layer on either side of the membrane results in the formation of pressure and concentration gradients near the membrane surface (addressed as concentration polarization) which reduces the driving force.

Scholz et al. (2012) have correctly highlighted the fact that conventional studies have generally ignored the process non-idealities and there exist very few studies which have studied the non-idealities such as concentration polarization (Ohlrogge et al., 2010), Joule–Thomson effect (Gorissen, 1987), real gas behaviors (Soni et al., 2009), and pressure drop on both sides of the membrane. Scholz et al. (2012) developed and validated a model considering concentration polarization, the Joule–Thomson effect, pressure losses, and real gas behavior. Their case-study on CO₂/propane and CO₂/methane showed that the non-ideality in the case of CO₂/methane was notable. This fact might be extendable to CO₂/N₂ mixtures. We expect that future research on gas membranes will focus more on addressing the process non-idealities.

With this background on the modeling of membrane unit, it would be interesting to know that except for very limited studies (e.g., Alshehri et al., 2013; Hasan et al., 2012; Khalilpour et al., 2012; Merkel et al., 2010), the mainstream PCC membrane modeling tasks have been carried out with assumption of binary CO₂/N₂ mixture for flue gas. We will address the binary studies in later sections when we review membrane systems and the techno-economic studies. Merkel et al. (2010) used multicomponent flue gas in their study, but did not present their model. Khalilpour et al. (2012), using the multicomponent gas model of Pan (1986), investigated the impact of numerous parameters such as area, length, pressure, permeance, and selectivity on the separation of CO₂ from flue gas over co/countercurrent hollow fiber membranes. From a merely technical point of view, they showed that when the concentration of CO₂ in the inlet feed is comparatively low (less than 15%), membrane separation, neither in pressurized nor in vacuum configurations, can satisfy high purity permeate or high recovery. Their study showed selectivity and permeability have a combined impact on PCC membrane performance and a high selectivity (e.g., >50) is not merely advantageous. A similar proposal was given earlier by Kaldis et al. (1998) who studied flue gas with binary CO₂/N₂ composition. Khalilpour et al. (2012) also identified optimal regions of flue gas pressures and membrane area within which a techno-economic process system design could be carried out. Alshehri et al. (2013) introduce a model by accommodating the Hagen–Poiseuille approximation formula in Shindo et al. (1985) in order to describe the permeate pressure change in the fiber lumen. With this model, they investigated the performance of a flue gas with four components (CO₂, N₂, O₂, and H₂O) over co- and countercurrent membrane configurations.

3.2. Multi-stage membrane network synthesis and design

There is general consensus that membranes are good for bulk separation. We can categorize membrane processes into two major groups:

- 1 When the concentration of the target component in the inlet feed gas is high, membranes can perform very well compared to other kinds of separation systems, resulting in high purity permeate. However, they fail in achieving a retentate stream with a low concentration of target component. One example is the case of a gas sweetening process for which membrane is an economical option to separate bulk of sour gas, whilst it is not capable of achieving a retentate (processed natural gas) with required pipeline specifications, i.e., sour gas concentration less than 2%. Therefore, a hybrid of membrane and amine system is introduced, in which the membrane takes the responsibility of the bulk of separation and the amine solvent further reduces the sour concentration of retentate.
- 2 When the concentration of the target component in the inlet feed gas is comparatively low, the membrane can neither satisfy high purity permeate nor low-concentration retentate.

In most of the flue gas cases, the concentration of CO₂ is notably low (Table 1). 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-economic investigations. The success of membrane systems will be very much dependent on process synthesis, configuration, and design. Here, we review the works on membrane process network (in general and for PCC processes) and we will discuss techno-economics in the next section.

As seen in many industrial applications, single-stage membrane separation has limitations in achieving high quality permeate or retentate while typically the objective of separation is either a high quality permeate or a high quality retentate. The reason is due to the permeation requiring a driving force between two membrane sides, i.e., $x_j P_f - y_j P_p > 0$, resulting in:

$$y_j < \frac{x_j P_f}{P_p} = \frac{x_j}{\beta}$$

Therefore, when the concentration of target component j in the feed gas (x_j) is low, even high pressure ratios (β) may not achieve high permeate purity (y_j). As such, more stages are required in order to achieve the desired quality and high recovery. The first solution was a patent by Pfefferle (1960) who presented a two-stage system with permeate recycled in order to reach high purity permeate. Following the two-stage presentation, a cascade of membrane systems was introduced for a binary gas mixture separation (Kakuta et al., 1978; Ozaki et al., 1978). Gruzdev et al. (1984) proposed a method for calculation of a cascade system when there is a multicomponent gas mixture. Moreover, some studies have proposed using different membrane materials in the cascade system (Stern et al., 1984).

The cascade model (shown in Fig. 6) is the most general multistage membrane design. The design idea is borrowed from conventional mass transfer operation designs such as multi-stage distillation or extraction systems (Treybal, 1955). The downstream membranes enrich permeate to higher purities of the target components while upstream membranes strip remaining traces of target components to desired values. In many processes, either of the enriching or stripping section is required. For instance, in the

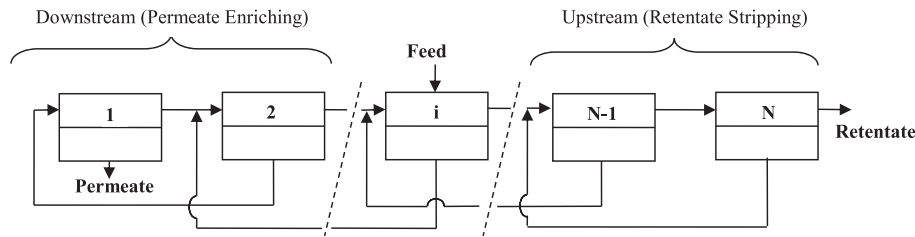


Fig. 6. Schematic of cascade membrane system with recycle.

case of oxygen separation from air via air separation units (ASU), the downstream enriching section is not required. In the case of natural gas sweetening, the objective is to minimize the concentration of sour gas (CO_2 and H_2S) in retentate. Therefore, an upstream stripping section is required. Moreover, the concentration of permeate, i.e., sour gas, is also important in order to minimize natural gas loss in the permeate stream. Therefore, a downstream stripping section is also needed.

It is, however, discussed that, except very low feed concentrations (Li et al., 1990) or low-efficient membranes (Avgidou et al., 2004), a series of two (Ozaki et al., 1978) or three stage (Pettersen and Lien, 1995) membrane system is usually the most techno-economically optimal configuration. It is proven that the introduction of more stages results in slightly less membrane area and compression energy, and the increase in the number of compressors ultimately neutralizes this advantage (Pettersen and Lien, 1995).

There have been numerous studies for optimal configurations of two/three-stage membrane systems. Studying the two-stage systems, Kao et al. (1989) compared the continuous column membrane, or CMC (Fig. 7a) (Pfefferle, 1960), to the two strippers in series permeator system, TSSP (Fig. 7b). They reported sweet-spot operating conditions for each configuration. According to them, TSSP is superior to CMC configuration unless the objective is to minimize membrane area or to have high purity permeate. A similar result was reported by Qiu et al. (1989), in terms of economic evaluation, stating that TSSP is the best configuration when the objective is high quality retentate, while in the case of high quality permeate, CMC is more efficient.

Bhide and Stern (1993) studied seven different one-, two-, and three-stage configurations with respect to minimum costs. They found that a three-stage system with a single permeation stage in a series with a two-stage permeation cascade with recycle (Fig. 8) was the best.

Pettersen and Lien (1995) studied the intrinsic behavior of several single-stage and multi-stage permeator systems. They also divided the multi-stage system into enriching and stripping cascades which could be two- or three-stages. According to them, if the objective is to have retentate with minimum concentration of a high permeable component, then the upstream section of the cascade (stripping) will be chosen. In the case of a high purity

permeate product, design downstream section (enriching) is the best choice. Datta and Sen (2006) techno-economically reviewed ten different one-, two-, and three-stage configurations and reported that the selection of the best configuration is highly related to feed quality, separation objectives, and market parameters.

It can be concluded that the selection of proper multi-stage systems is highly dependent on the separation strategy which is mostly affected by economical inputs. When the retentate is the target product and its partial loss with permeation is not economically important, the strategy will be mere stripping. For mere stripping objectives, a two-stage (Fig. 7b) or three-stage (Fig. 9a) stripper would be selected. However, when the objective is high purity permeate, the strategy will be to enrich and a two/three-stage enriching system (Fig. 9b) will then be chosen.

There might be a condition where high quality retentate is required, but minimum loss in permeate is also desired. Alternatively, high quality permeate might be required with minimum loss in the retentate stream. In such conditions, when both high quality permeate and retentate are desired, a combination approach could be Fig. 7a (Pfefferle, 1960), Fig. 8 (Bhide and Stern, 1993), or Fig. 10 one-stage enriching with two-stage stripping (Pettersen and Lien, 1995). According to Seader and Henley (2006), the best method in designing cascade systems is to choose parameters in a way that the composition of a permeate recycled to any stage i is identical to that of feed entering the same stage.

Attention to multistage membrane network has taken off in recent years. There have been numerous efforts to develop so-called “superstructures” for membrane process synthesis (Agrawal, 1996; Qi and Henson, 2000; Uppaluri et al., 2004; Saif et al., 2009; Alshehri et al., 2013; Gassner and Maréchal, 2010).

The earliest study, was that by Vandersluijs et al. (1992) who investigated the merits of single-stage and two-stage cascade membrane systems for PCC application. They used the Shindo et al. (1985) model for membrane unit modeling with the assumption of binary CO_2/N_2 flue gas. They reported that for high purity CO_2 products (>80%), the two-stage system can notably outperform the single-stage process. Similar results were reported by Carapellucci and Milazzo (2003) who highlighted that the two-stage design is the best option for enriching CO_2 stream while the addition of the third stage does not notably improve the CO_2 purity while increases the process complexity markedly.

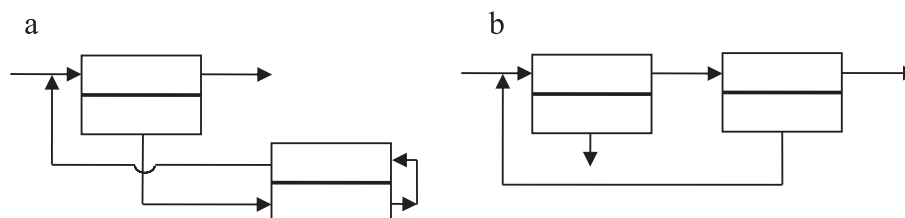


Fig. 7. Schematic of a) CMC and b) TSSP.

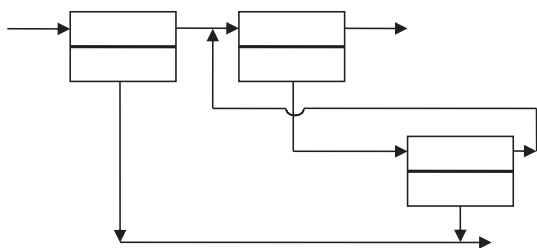


Fig. 8. Schematic of a single permeation stage in series with two-stage permeation cascade.

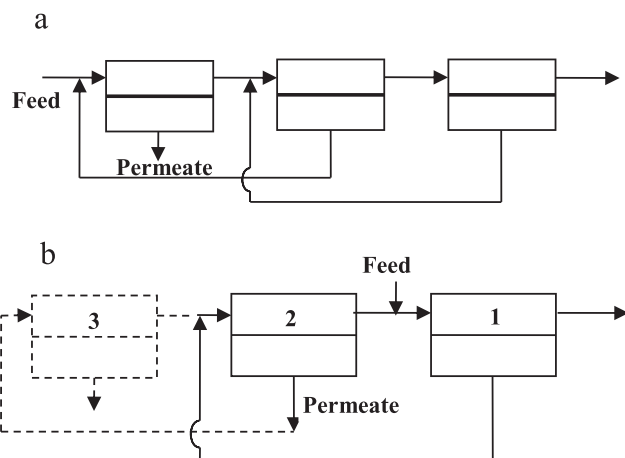


Fig. 9. Schematic of a) a three-stage stripping and b) a two/three-stage enriching system.

Ho et al. (2008a) investigated three processes, i.e., a single-stage and two-stage cascades with and without retentate recycle. They studied both vacuum and pressurized scenarios for single-stage while for two-stage processes only the vacuum scenario was studied. They employed the Shindo et al. (1985) model for developing a binary cross-flow gas separation model of the membrane unit. According to their results, the vacuum two-stage with retentate recycle could achieve the highest CO₂ purity, while in terms of cost and without considering purity, vacuum single-stage was the best.

Hussain and Hägg (2010) simulated two process configurations with facilitated transport membranes in an Aspen Hysys environment. The first configuration was a two-stage process with sweep gases of water vapor at the first stage (vacuum mode) and permeate at the second stage. The second configuration used recycled permeate as sweep gas for both stages. The result showed that the former configuration had a better performance. Merkel et al. (2010) also introduced a two-stage and two-step membrane system considering countercurrent flow at vacuum mode and using incoming combustion air as a sweep gas to generate driving force. In their process, the flue gas first goes under a two-stage membrane

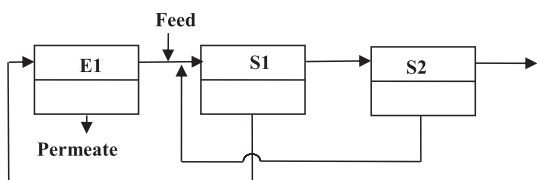


Fig. 10. Schematic of one-stage enriching with two-stage stripping.

with permeate recycle. In the second step, the CO₂-enriched air is then cooled to room temperature to remove the water content. The dry gas is then subcooled to around -20°C and sent to fractionation unit. The fractionation bottom is liquid CO₂ ready to be pumped and sent for sequestration. The overhead gas is mainly incondensable nitrogen and some CO₂. This gas stream goes into the third membrane unit where the CO₂ is further removed and recycled to the front of the membrane unit while the retentate is vented.

The idea of combustion air sweep was also utilized by Zhai and Rubin (2013b) who investigated a two-stage, two-step membrane system with air sweep for capturing CO₂ at coal-fired power plants. In the second step, the retentate passes through a membrane with sweep air flow to further dilute the flue gas before being vented.

Alshehri et al. (2013) introduced an *N*-stage membrane network superstructure considering possible flowsheet configurations. An optimization formulation was then developed and solved using an objective function that minimizes the costs associated with operating and capital expenses. The membrane unit model was developed using the Shindo et al. (1985) multicomponent gas model with the addition of pressure drop formulations inside the fiber. The model was able to synthesize the network configuration and identify the optimal design and operation variables. Their case study for a 300 MW coal-fired power plant resulted in a two-stage membrane system for CO₂/N₂ selectivity of 100 and a three-stage for selectivity of 50.

3.3. Discussion on membrane systems

A single-stage membrane is not a feasible solution for MPCC due to low CO₂ content of flue gas (Table 1), though it has been widely used in the modeling works for MPCC. The other issue is the significant impacts of other flue gas components on process system design while the mainstream studies are based just on the binary CO₂/N₂ assumption. Furthermore, some studies assume a mixed flow pattern that may be subject to error, as in practice cocurrent and countercurrent flows are used. There seems a general consensus in the literature on the positive impact of vacuum configuration and the application of sweep gas for MPCC.

4. Techno-economics of MPCC systems

A number of techno-economic studies have been carried out to evaluate the feasibility of membrane systems for removing CO₂ from flue gases and improve the viability of membrane technology for carbon capture. An early study by Vandersluijs et al. (1992) investigated the technical feasibility and mitigation costs of polymer membranes for the recovery of CO₂ from flue gases of a power plant. They employed a cross-flow permeation model in conjunction with optimization analysis for the membrane process to determine CO₂ abatement costs that depend on the separation targets. For the 50% product purity and 75% recovery for CO₂, the minimum achievable cost was estimated to be US\$48 per tonne of CO₂ avoided. Improving the product purity and the degree of CO₂ recovery to the higher levels of 95% and 90% respectively would significantly increase the cost of CO₂ avoided by nearly 50% (US\$71 per tonne of CO₂ avoided). They illustrated that for the membranes available at the time of their study, membrane capture technology could not compete with solvent-based technologies; and in order for membranes to become economically attractive for carbon capture, membranes with CO₂/N₂ selectivity higher than 200 along with high permeability would be required. This threshold value regarding the selectivity has thereafter been cited by different membrane studies (Aresta, 2003; Favre, 2007; Feron et al., 1992; Wolsky et al., 1994).

Kazama et al. (2004) carried out an economic analysis to evaluate their developed Cardo polyimide hollow fiber membrane with high CO₂ permeance of 1000 GPU and CO₂/N₂ selectivity of 40. They illustrated that the success of membranes as an alternative to existing amine-based capture systems depends on the CO₂ concentration of source gases. When the inlet CO₂ concentration is around 25% or more, membrane systems become economically advantageous over amine-based capture systems. In addition, the energy penalty of vacuum pumping for producing the driving force for gas separation would contribute 50% or more of the total separation cost, which implies that reducing the power use for the capture process would help lower the cost for removing CO₂ from flue gases. Membrane capture systems, therefore, become more viable with pressurized gas streams via reducing the energy requirement for gas separation.

Matsumiya et al. (2005) estimated energy consumption of a novel ultrafiltration hollow fiber module with facilitated transport membrane for the separation of CO₂ from the flue gas and evaluated the effects of a range of major parameters including the permeate side pressure, temperature, gas and liquid flow rates, and the inner diameter of hollow fiber membranes. In the membrane module, both the flue gas and carrier solution (DEA) are supplied to the lumen side (slightly above atmospheric pressure) of the hollow fiber membrane, and CO₂ is dissolved in the carrier solution and permeates. As soon as the solution enters the shell side, being under vacuum pressure, CO₂ is liberated and the solution is recycled. Among the key parameters, increasing the inner diameter of the hollow fiber would remarkably decrease the energy penalty. The energy consumption was reported to be in the range from 0.072 kWh/kg-CO₂ (0.259 GJ/tonne-CO₂) to 0.211 kWh/kg-CO₂ (0.796 GJ/tonne-CO₂) when the hollow fiber inner diameter was changed from 1.4 mm to 0.8 mm. In addition, they evaluated two different designs for achieving the required driving force between feed and permeate sides. In one design the flue gas entering the feed side was compressed while the permeate side was kept under the atmospheric pressure. In contrast, the other design kept the feed flue gas under the atmospheric pressure but made a vacuum condition in the permeate side. They found that the energy consumption required for achieving the driving force using the vacuum strategy was significantly less than the one with compressing the feed flue gas. A similar conclusion was made by Zhai and Rubin (2013b) based on the analysis for two-stage membrane systems.

Bounaceur et al. (2006) systematically conducted parametric analyses to identify the potential as well as the limitations of single-stage membrane separation processes for CO₂/N₂ separation in comparison with amine-based solvent processes. Amine absorption is shown to be the best option when a high CO₂ purity is desired as the high purity induces a large energy penalty for membrane systems. However, when the CO₂ recovery ratio and permeate composition do not exceed 0.8 and the CO₂ concentration of flue gas is more than 20%, the membrane separation has significant advantage over amine absorption because of its lower energy requirement of about 0.5–1 GJ/tonne-CO₂ recovered. This study concluded that for the membranes with CO₂/N₂ selectivities less than 50, the membrane process is not feasible and higher selectivities more than 100 are required to facilitate the feasibility for carbon capture. Similarly, another study also claimed that MEA-based capture technology is less expensive than membrane capture technology even for CO₂ purity requirements as low as 60% (Ho et al., 2006b).

Ho et al. (2006a) compared the feasibility of a single-stage membrane process for PCC against an amine-based system and examined the effects of membrane characteristics, operating parameters, and system design on sequestration costs. They used the Shindo et al. (1985) model considering binary flue gas and

evaluated three membranes: Poly (phenylene oxide) (PPO), Polyimide (PI), and PEO. The three membranes have CO₂/N₂ selectivities of 20, 30, and 50, respectively, resulting in a total sequestration cost of US\$55 to 61/tonne CO₂ avoided. Their techno-economic assessment confirmed the general consensus that such membrane selectivities require a high feed gas compression rate, which makes membranes not economically competitive against MEA systems. They suggested several approaches to improve the viability of membrane technology, including improvements in CO₂ permeability and selectivity and changes to the process configurations and operating pressures as well as reductions in the cost of membranes.

Favre (2007) offered a critical comparison of dense polymeric membrane processes with amine absorption for post-combustion carbon capture and addressed that the potential of dense polymeric membranes to solve the flue gas treatment problem may have been underestimated. Although membranes in conjunction with a single-stage module, even with CO₂/N₂ selectivity as high as 120, cannot compete with amine absorption for low CO₂ content, flue gases such as those from power plants, may compete with amines for application to flue gas sources with high CO₂ concentrations above 20% (such as flue gas from cement or steel production). That paper also comparatively presented the Robeson plots revealing the tradeoff between permeability and selectivity for rubbery and glassy polymers and showed that rubbery polymers may have relatively higher potential for flue gas treatment. However, both of the upper bound lines appear somewhat more optimistic than the similar ones presented by others (Bernardo et al., 2009; Powell and Qiao, 2006; Scholes et al., 2008).

Ho et al. (2008a) also compared the two major strategies of producing the driving force for membrane gas separation at coal-fired power plants: compressing feed gas stream versus vacuum pumping in the permeate side, which is similar to other studies (Bounaceur et al., 2006; Matsumiya et al., 2005). They showed that while the vacuum strategy required relatively high membrane area, it could achieve 35% less capture cost per tonne of CO₂ avoided, compared to the compression design. But, neither of the driving force designs could result in a capture cost competitive with amine solvents.

Zhao et al. (2008) investigated the effects on membrane performance (CO₂ separation degree and CO₂ purity) of operating conditions (e.g., CO₂ concentration in the flue gas, pressure and temperature, etc.) as well as membrane properties (permeability, selectivity) and membrane area. They modeled a single-stage membrane process and also found that the single-stage membrane process could not achieve high purity CO₂ and separation degree at the same time.

Merkel et al. (2010) reported development of a new membrane with CO₂ permeances of greater than 1000 GPU and a CO₂/N₂ selectivity of 50 at 30 °C, which has permeance 10 times higher than those of commercial CO₂ membranes, but has a selectivity within the range reported for non-facilitated transport materials. They developed a novel two-stage membrane system using combustion air as sweep gas that carries a portion of permeated CO₂ back to the boiler and finally increases the CO₂ concentration of flue gas into the capture unit. Their study claimed that the membrane process with combustion air sweep for 90% CO₂ capture would account for 16% of the power output of a coal-fired power plant and result in a capture cost as low as \$23/tonne CO₂. Their study also suggested that improving the CO₂ permeance may become more important than increasing the CO₂/N₂ selectivity to reduce the overall cost.

Hussain and Hägg (2010) used a novel CO₂-selective facilitated transport membrane (PVAm) with selectivity of 200 in their techno-economic study. They compared two-stage membrane

processes with amine absorption in terms of energy requirement. They reported that membrane process using the facilitated transport membrane is feasible, even for low CO₂ concentration (10%) in flue gas while achieving more than 90% CO₂ purity and recovery.

Zhai and Rubin (2013b) evaluated the performance and costs of multiple membrane capture systems including single- and multi-stage configurations on a common framework. Multi-stage membrane systems were identified to be able to simultaneously achieve the 90% removal efficiency and 95% or more product purity for CO₂ at pulverized coal power plants. The comparative assessment results indicate that the multi-stage membrane system with combustion air sweep is capable of achieving the separation targets at an avoidance cost that is 15% less than that of an amine-based capture process. Consistent with the finding by Merkel et al. (2010), enhancing the CO₂ permeability of membrane materials appear to be more economically attractive than increasing the CO₂/N₂ selectivity. However, they also highlighted a few key caveats such as the influences of minor gas components and humidity on membrane performance.

4.1. Discussion on MPCC economics

The utilization of diverse membrane process models (simplified or rigorous) might be one of the main sources of discrepancies amongst the techno-economic studies, whilst efficient general models already exist in the literature. Therefore, it appears necessary that future studies employ more rigorous models for techno-economic assessments.

More importantly, though technical and cost studies along with optimization analyses have been conducted actively for membrane capture systems, the costing scope and methodology appear inconsistent across existing studies (Zhai and Rubin, 2013b), which makes it hard for cost comparisons among different membrane materials and process designs. There are big differences in the capital costing scope across various studies. Many cost studies include direct cost components such as membrane module, support framework, and power equipment, but largely ignore such indirect capital costs as process and project contingencies and owner's costs, which can account for more than 40% of total capital cost. As one of the key cost components of a CCS (carbon capture and sequestration) system, CO₂ product compression is not included in the scope of some techno-economic studies that evaluate the feasibility of membrane capture systems. The cost metric of "cost of CO₂ captured" has been adopted by many membrane studies, but this measure typically employs arbitrary electricity price assumptions that vary by more than a factor of two across existing studies, which is inappropriate for reporting and comparing CCS costs because of the big energy requirement of CCS systems (Zhai and Rubin, 2013b). Rubin et al. (2013) proposed a common costing methodology and provided detailed guidelines to improve the clarity and consistency of CCS cost estimates.

Furthermore, the deployment of CCS in fossil fuel-fired power plants likely will start with partial CO₂ capture. In September 2013, the U.S. Environmental Protection Agency proposed emission performance standards to limit CO₂ emissions from new fossil fuel-fired power plants. The compliance with the proposed emission performance standards would require roughly 40–50% CO₂ capture for new pulverized coal power plants, depending on plant designs (Zhai and Rubin, 2013a). However, in the existing studies, the process designs and economics evaluation of membrane capture systems have been focused heavily on the 90% CO₂ capture efficiency. Although some studies have evaluated partial CO₂ capture, the CO₂ product of membrane capture processes has a lower purity less than 90–95%, which is not suitable for transport and geological storage. In addition, the existing cost comparisons for membrane-

versus amine-based CCS systems are basically limited to the 90% CO₂ capture efficiency. However, the costs of CO₂ avoided or captured by two types of CCS systems appear different trends as a function of CO₂ capture efficiency. For a typical amine-based capture system, the cost-effective CO₂ capture often happens to the 90% removal efficiency. In contrast, the minimum cost of CO₂ captured by a two-step/sweep membrane process is at about 70% of removal efficiency (Merkel et al., 2010). Therefore, more careful process development and economic assessments are needed for membrane systems designed for partial CO₂ capture.

5. Conclusion

There has been an increasing interest in the application of membranes as an alternative technology in post-combustion carbon capture (PCC). Historically, there has not been a general agreement on the advantage of membranes against other methods such as amine-based absorption–desorption processes for CO₂ capture. In this paper, we reviewed the progress of membrane based PCC (MPCC) from both material and process design perspectives plus engineering economics.

The research on polymeric membranes for carbon capture likely move towards improving their performance by incorporating additional agents into the polymeric phase that could be another polymer (polymeric blends), particulate matter (mixed matrix membranes), or a carrier molecule (facilitated transport). Facilitated transport membranes (e.g., PVA based) seem to be promising for carbon capture. Membrane gas contactors have been suffering from the additional mass transfer resistance. However, a number of approaches to modify membrane materials are being investigated to improve the performance of gas absorption membranes. These include: plasma treatment, applying a thin hydrophobic layer to base membrane materials, incorporation of salts into the membranes during manufacture, and changing manufacturing parameters to alter membrane characteristics such as pore diameter.

Permeability and selectivity are two critical attributes of a good membrane. An industrially desirable membrane, however, 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 permselectivity 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 ignored widely in the literature and the existing studies, 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 in various perspectives.

The widely used single-stage membrane configuration is not a feasible solution for MPCC due to the low CO₂ content of flue gas, even for membranes with high permselectivities. In the literature, there is an agreement with the positive impact of vacuum configuration in reducing the system energy penalty. Multi-stage membrane systems are feasible to simultaneously achieve the separation targets of high product purity and high removal efficiency for CO₂. To improve the membrane technology's viability, optimizing the design of driving force for membrane gas separation appears important to reduce the energy penalty and the capture cost for membrane capture systems. Although recycling a portion of captured CO₂ via the gas sweep design may increase the CO₂ partial pressure of feed flue gas, and in turn, remarkably reduce the system power use, the effects of CO₂-rich air combustion on traditional boiler performance and other environmental control systems

remain unclear, which needs more careful analyses. Many existing studies only evaluate the performance and costs of membrane capture systems alone, but do not explore the relations of power generation system designs to the process parameters and material properties that influence the overall performance and cost of membrane capture technologies. A plant-level analysis is needed to help explore tradeoffs in meeting performance and cost objectives and identify the most promising system designs and R&D targets of material properties for advancing membrane capture technologies.

The differences in gas separation and process models (multi-component versus binary, multi-stage versus single-stage, etc.) employed by existing membrane studies are considered to be one of the key sources of discrepancies amongst the techno-economic studies. Furthermore, the costing scope and methodology appear inconsistent across existing studies and application of a common costing methodology could improve the clarity and consistency of MPCC cost estimates.

List of abbreviations

ASU	air separation units
BAT	best available technology
BAS	bis(aminopropyl)polydimethylsiloxane
CA	cellulose acetate
CAPEX	capital and operational expenditure
CCS	carbon capture and sequestration
CMC	continuous membrane column
CRGT	chemically recuperated gas turbine
DADE	diamino diphenyl ether
EOR	enhanced oil recovery
GPU	gas permeation unit
IPCC	Intergovernmental Panel on Climate Change
LDPE	low-density polyethylene
MEA	monoethanolamine
MGC	membrane gas contactors
MMD	membrane material design
MPCC	membrane-based carbon capture
MSE	membrane systems engineering
MTMS	methyltrimethoxysilane
OPEX	operational expenditure
PA	polyamides
PAA	poly(allylamine)
PCC	post-combustion carbon capture
PE	polyethylene
PEO	poly(ethylene oxide)
PEP	poly(epichlorohydrin)
PES	polyethersulfones
PI	polyamides
PP	polypropylene
PTFE	polytetrafluoroethylene
PU	polyurethanes
PVA	poly(vinyl alcohol)
PVDF	poly(vinylidene fluoride)
SLM	support liquid membranes
SPBI	sulfonated polybenzimidazole
TCDA	alicyclic 2,3,5-tricarboxy cyclopentyl acetic dianhydride
TSSP	two stripper in series permeator
UN-FCCC	United Nations Framework Convention on Climate Change
VDF	vinylidene fluoride

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