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A review of material development in the field of carbon capture and the application of membrane-based processes in power plants and energy-intensive industries

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Abstract

This review highlights recent developments and future perspectives on CO_2 capture from power plants and energy-intensive industries to reduce CO_2 emissions. Different types of membrane materials for CO_2 capture were reviewed in terms of material performance, energy efficiency, and cost. With regard to gas separation membrane technology, only three types of membranes have been demonstrated at pilot scale. Therefore, this work paid particular attention to recent development of membrane materials such as fixed-site-carrier membranes and ultrathin nanocomposite membranes. The required high-performance membranes with CO_2 permeance of 3 m^3(STP)/ (m^2 h bar) and high CO_2/N_2 selectivity (> 40) were identified as the future direction of material development. Moreover, novel energy-efficient process development for CO_2 capture in power plant and process industry are discussed; the MTR patented air sweeping process is considered one of the most energy-efficient processes for post-combustion CO_2 capture. In the last part, CO_2/CH_4 selectivity of > 30 was pointed out to be the requirement of energy-efficient membrane system for CO_2 removal from natural gas and biogas. Finally, significant improvements on membrane material performance, module, and process efficiency are still needed for membrane technology to be competitive in CO_2 capture.

Keywords: CO_2 capture, Membrane, Flue gas, Post-combustion, Natural gas, Biogas

Introduction

The International Energy Outlook [79] (IEO2011) reference case reported that world energy-related carbon dioxide (CO_2) emissions would increase to 35.2 billion metric tons in 2020 and 43.2 billion metric tons in 2035. Control of anthropogenic emissions of greenhouse gases (GHG), especially CO_2, is one of the most challenging environmental issues related to global climate change. Three different solutions can be employed to reduce CO_2 emissions, i.e., improving energy efficiency, switching to use less carbon-intensive and renewable energy, and carbon capture and storage (CCS). Among them, CCS is considered as one of the most promising way which can continuously use fossil fuels without causing significant increase of CO_2 emissions. The main applications of CCS are likely to be at large CO_2 point sources: fossil fuel power plants and energy-intensive industries such as iron/ steel manufacture, refinery, cement factory, and natural gas and biogas plants [1]. Among them, fossil fuel power plants are responsible for the largest CO_2 emissions, and post-combustion power plants are being the main contributors which need to be firstly tackled. Moreover, CO_2 removal from natural gas or biogas is also mandatory as the acid gas can cause pipeline corrosion during gas transportation. CO_2 capture from exhaust gases in cement factory receives particular attention as CO_2 is also a byproduct in a cement production process and cannot be avoided.

Different technologies such as chemical and physical absorption, membrane separation, physical adsorption, cryogenic distillation, and chemical looping can be used for CO_2 capture in various processes [76]. The conventional chemical absorption is a mature technology for CO_2 separation, but is also energy intensive and high cost, which can result in a large incremental cost and a significant

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environmental impact. Membrane technology has already been commercialized and documented as a competitive technology for selected gas separation processes such as air separation and natural gas sweetening during the last two or three decades. Great effort has been recently placed on CO_2 capture using gas separation membranes, and examples are found in the literature [16, 22, 27, 28, 32, 33, 50, 77, 101, 127, 137, 158]. However, there are still challenges on the applications of membranes for CO_2 capture related to (1) the limitation of membrane separation performance (the trade-off of gas permeance and selectivity of most polymeric membranes) and (2) the poor membrane stability and short lifetime when exposing to a gas stream containing the impurities of acid gases such as SO_2, NO_x. Thus, high-performance membranes with low material cost and high stability should be developed. MTR (Membrane Technology & Research, Inc.) tested their high permeable ultrathin Polaris™ membranes for CO_2 capture in a 1-MW coal-fired power plant with a large pilot system. Moreover, high-performance fixed-site-carrier (FSC) membranes were developed by the NanoGLOWA project (EU FP6) for CO_2 separation. A small pilot-scale system was tested in 2011 for CO_2 capture from flue gas at Sines coal-fired power plant in Portugal (developed by the Membrane Research team (Memfo) at NTNU), and the stable performance over 6 months was reported [138], and their latest pilot system with 20-m^2 hollow fibers were tested for CO_2 capture in Norcem cement factory [51]. In addition, a 10-m^2 PolyActive® membrane module developed by Helmholtz-Zentrum Geesthacht was also tested for CO_2 capture [119]. Those efforts have brought membrane technology for post-combustion CO_2 capture to a higher TRL (technology readiness levels). Moreover, some emerging separation technologies based on the novel solvents of ionic liquids (high CO_2 solubility) and microporous materials (solid adsorbents) of zeolite, metal organic frameworks (MOFs), and metal oxides (chemical looping cycle) have been recently developed for CO_2 capture and showed a nice potential and cost reduction benefit [17, 26, 67, 76, 95, 136, 162, 164]. It should be noted that those advanced materials are mostly in the early research phase, and material cost together with upscaling issue need to be further investigated. In this work, the main focus is to provide an overview of the latest development and progress of membrane materials (especially some membranes at high TRL) and membrane-based processes for CO_2 capture from power plants and energy-intensive industries (e.g., cement factory, biogas, and natural gas plants).

Membrane materials for CO_2 capture
Each membrane material has its own advantages and challenges related to material cost, separation performance, and lifetime. Development of advanced membrane materials to increase cost-effectiveness is crucial to bring down CO_2 capture cost. Different membranes such as polymer membranes, microporous organic polymers (MOPs), FSC membranes, mixed matrix membranes (MMMs), carbon molecular sieve membranes (CMSMs), and inorganic (ceramic, metallic, zeolites) membranes can be used for CO_2-related separation [76]. Each membrane material possesses its own separation property, thermal and chemical stability and mechanical strength. In general, most polymer membranes show good separation performance and relatively low cost, but a relatively low membrane stability by exposure to acid gases and adverse conditions (high temperature and pressure). Inorganic membranes can be operated in these adverse conditions, but module construction and sealing for high-temperature application are quite challenging, and production cost is usually much higher compared to polymer membranes. Novel membrane materials especially FSC and MMMs (summarized in Table 1) attract great interest in the membrane community, which are based on either an enhanced facilitated transport mechanism or combination of both polymeric and inorganic material properties. Thus, choosing a suitable membrane material for a specific application mainly depends on membrane material properties, feed gas composition and flow rate, process operating conditions, and separation requirements [123]. Recently, membrane performance has been significantly improved owning to the great effort that has been taken from the membrane community. Wang et al. [151] summarized the status of single-stage membrane performance in the upper bound plots for CO_2/N_2 and CO_2/CH_4, and most ultrathin polymer membranes stayed closer to both upper bounds compared to the commercial polymers, which indicated the great potential for carbon capture applications. It should be noted that some membranes like the MTR Polaris™ membranes and the FSC membranes (patented by NTNU) have already been demonstrated at pilot scale [51, 106] and are quite promising for CO_2 capture from flue gas due to their high performance and good stability when exposed to a flue gas containing the impurities of SO_2 and NO_x.

Polymer membranes
Polymer membranes have been widely used for selected commercial gas separation processes due to their good separation performance, good mechanical stability, and low cost. Most membrane systems for gas separation use glassy polymers because of their high selectivity and good mechanical properties, and polyimide membranes exhibits excellent high selectivities combined with high permeances for a large variety of applications in gas separation [41], while some rubbery polymers are also used for specific vapor/gas separation processes based on gas solubility difference in membrane materials, e.g., volatile

Table 1 Representative FSC membranes and MMMs for gas separation

Material	Support	Membrane module	Gas separation	Reference
FSC membranes				
Poly(amidoamine)/poly(vinyl alcohol)	–	Flat sheet	CO_2/H_2	[37]
Polyallylamine (PAAm)/poly (vinyl alcohol) (PVA) blend	Polysulfone	Flat sheet	$CO_2/H_2/N_2/CO$	[166]
PVAm & PVAm/PVA blend	Polysulfone, polyphenylene oxide (PPO)	Flat sheet, Hollow fiber	CO_2/N_2, CO_2/CH_4	[31, 71, 74, 86, 87, 147, 148]
PVA	–	Flat sheet	$CO_2/H_2/N_2$	[77]
	–	Flat sheet	CO_2/CH_4	[80]
CNT-reinforced PVAm/PVA blend	Polysulfone	Flat sheet	CO_2/CH_4	[62, 63, 66–69]
Nanotube-reinforced PVAm	Polyethersulfone (PES)	Flat-sheet	CO_2/N_2	[58]
High temperature ionic liquids	Nylon	Flat sheet	CO_2/H_2	[110]
Room temperature ionic liquids (RTILs)	polyvinylidene difluoride (PVDF)	Flat sheet	CO_2/air, SO_2/air, $CO_2/N_2/H_2$	[102, 112]
MMMs				
Polymer matrix	Inorganic filler	Membrane module	Gas separation	Reference
Poly(vinyl acetate) (PVAc)	Zeolite 4A, TiO$_2$	Flat sheet	CO_2/N_2	[2–4]
PIMs	ZIF-8, CNTs	Flat sheet	H_2/N_2, H_2/CH_4, He/N_2, O_2/N_2 CO_2/CH_4	[21, 82]
Poly (ethylene oxide) (PEO)	Graphene oxide	Flat sheet	CO_2/N_2	[122]
Pebax	1 D multi-walled CNT/ graphene oxide nanoribbon	Flat sheet	CO_2/N_2, CO_2/CH_4	[114]
PIMs	MOFs	Flat sheet	CO_2/N_2	[44]

organic compounds (VOCs) recovery and hydrocarbon recovery from natural gas. Commercial polymeric gas separation membranes are mostly made from cellulose acetate (UOP, GMS, NATCO), polysulfone (Air Products), and polyimides (Praxair), polyphenylene oxide (Parker-Hannifin), and polydimethylsiloxane (GKSS, MTR).

Gas permeability and selectivity are the two key parameters for the characterization of separation performance of dense polymer membranes, which should be as high as possible to achieve separation requirements at a low cost. However, gas permeability is mainly dependent on a thermodynamic factor (solubility (S) of penetrates in a membrane) and a kinetic factor (diffusivity (D) of the gas species transport through a membrane) [7]. Thus, there is a trade-off between permeability and selectivity in the dense polymer membranes as reported by Robeson [129]. The polymer membranes based on a solution-diffusion (S-D) transport mechanism cannot surpass the Robeson upper bound to achieve a higher permeability/selectivity combination unless the membranes involve other transport mechanisms such as molecular sieving and facilitated transport, or have large porosity and fractional free volume (FFV).

Microporous organic polymers

Strong interests have been put on the development of microporous organic polymers due to its large surface area. The representative MOPs include thermally rearranged (TR) polymers [35, 57, 85, 115, 116] and polymers of intrinsic microporosity (PIMs) [5, 18–20, 36, 104, 144, 160]. Polyimide-based TR polymers with an average pore size 0.4–0.9 nm and a narrow pore size distribution was firstly prepared by Park et al. [116], which presented a molecular sieving transport mechanism for gas permeation. The flexible structures provided the feasibility and the easiness for module construction. Moreover, TR polymer membranes were also found to exhibit excellent gas separation performance for CO_2-related separation processes, for examples, CO_2/CH_4 separation in high-pressure natural gas sweetening process [35, 115] and high temperature H_2/CO_2 separation in pre-combustion process [57]. However, most of the efforts are still focused on the development of lab-scale films of TR membranes, only a few literature reported that fabrication of hollow fiber TR membranes [84, 92, 154]. Kim et al. prepared their lab-scale TR-PBO (polybenzoxazole) hollow fiber membranes with a CO_2 permeance of 1938 GPU (1GPU = 2.736×10^{-3} m^3(STP)/(m^2 h bar)) [84],

but the CO_2/N_2 selectivity of 13 should be further improved. Woo et al. reported a superior CO_2 permeance of ~ 2500 GPU with a moderate CO_2/N_2 selectivity of 16 of the TR-PBO hollow fibers with ultrathin defect-free skin layer [154], which might be suitable for bulk CO_2 removal from flue gas.

Another type of microporous polymer materials of PIMs attracted great interest due to their relatively slow physical aging, high gas permeability, and high selectivity compared to poly(1-trimethylsilyl-1-propyne) (PTMSP) membranes that initially formed microporous structures are rapidly corrupted [36]. PIMs showed a high surface area (600–900 m^2/g) as reported by Budd et al. [18] and a high fractional free volume (22–24% [105]) which is comparable to that of PTMSP membranes (32–34.3% [109, 120]). Du et al. reported that PIMs functionalized with CO_2-philic pendant tetrazole groups (TZPIMs) can further improve CO_2 permeance by increasing CO_2 solubility due to the strong interaction between CO_2 and N-containing organic heterocyclic groups [36]. Their results indicated that CO_2/N_2 separation performance of TZPIMs can potentially surpass the Robeson upper bound. Moreover, a systematic review on preparation, characterization, and application of PIMs has been conducted by McKeown [104]. They pointed out that composite membranes consisting of PIMs and other polymers can present higher gas separation performance.

Fixed-site-carrier membranes
FSC membranes for CO_2 separation attracted great attention due to the high CO_2 permeance and selectivities of CO_2 over other gas species (e.g., N_2 and O_2). The carriers (amino functional group, -NH_2) are chemically bonded onto the polymer main chain. Thus, the FSC membranes usually present a higher stability compared to supported liquid membrane (SLM) and emulsion liquid membrane (ELM). Tong et al. conducted a review on facilitated transport membranes related to transport mechanism and

materials [145]. The gas transport through a facilitated transport membrane is illustrated in Fig. 1, where the CO_2 molecules react with amino functional groups when water is available, and pass through FSC membranes based on the combination of S-D and facilitated transport (FT) mechanism, while the non-reactive gas molecules (e.g., N_2, O_2) can only transport via S-D mechanism as documented by Kim et al. [86]. The gas permeate flux of the reactive component A (such as CO_2) will be the sum of both solution-diffusion and carrier-mediated diffusion (i.e., facilitated transport), which can be expressed as follows [86, 117]:

$$J_A = \frac{D_A}{l}\left(c_{A,0} - c_{A,1}\right) + \frac{D_{AC}}{l}\left(c_{AC,0} - c_{AC,1}\right) \quad (3)$$

where D_A and D_{AC} are diffusion coefficient of the Fickian diffusion and the carrier-mediated (complex) diffusion, respectively. l is the thickness of the selective layer. Feed pressure is crucial to get high flux by enhancing the contribution from both S-D and FT. However, after the carrier saturation, further increasing feed CO_2 partial pressure will not enhance the FT contribution. Thus, the trade-off between energy consumption and reduced membrane area (with increased flux) should be identified to determine the optimal operating condition [75]. A moderate feed pressure (e.g., 2.5–3 bar) was recommended as the optimal operating condition for the FSC membranes [64]. Table 1 shows some representative facilitated transport membranes that have been reported in the literature. Among them, the polyvinyl amine (PVAm)-based FSC membranes patented by the Memfo team at NTNU shows the highest CO_2 permeance (up to 5 m^3 (STP)/(m^2·h·bar)) and CO_2/N_2 (> 500) selectivity under humidified conditions [87]. This membrane is extremely promising for post-combustion CO_2 capture where flue gas is usually water vapor saturated [61, 64, 87]. A pilot flat-sheet FSC membrane system has been tested in EDP's power plant in
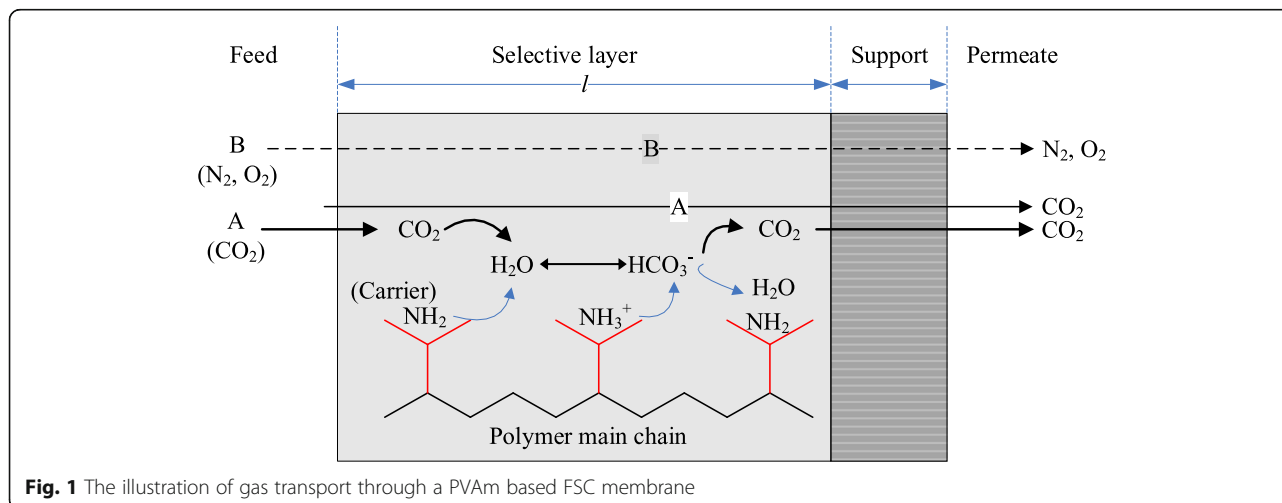

Fig. 1 The illustration of gas transport through a PVAm based FSC membrane

Sines (Portugal) in 2011, and the membranes showed a stable performance over 6 months [52]. Later on, the hollow fiber FSC membranes were tested at Sintef CO_2 lab at Tiller (Norway) with a 9.5% CO_2 contained flue gas produced from a propane burner [74]. They reported that single-stage membrane system (area 8.4 m^2) can achieve > 60% permeate CO_2 purity at a feed and permeate pressure of 2 bar and 0.2 bar, respectively, and the system also showed quite fast response when changing feed CO_2 composition. The reported pilot FSC membrane system provided great flexibility on testing the influence of process operating parameters, especially temperature. However, the challenges related to the optimization of module and process should be further investigated. In addition, material development by introducing other support and more effective multi-amines and aminoacids with higher CO_2 reaction kinetics and loading capacity is crucial to further improve membrane performance. Han et al. recently reported a nanotube reinforced 2-(1-piperazinyl) ethylamine sarcosinate blend with PVAm composite membrane with 1451 GPU CO_2 permeance and 165 CO_2/N_2 selectivity at 65 °C [58], which will be very promising if such performance can be achieved in field testing.

Mixed matrix membranes

Rigid permeable or impermeable particles are dispersed in a continuous polymeric phase to form MMMs to present interesting materials for improving separation performance of common polymer membranes [6]. Two types of inorganic fillers can be added into polymer matrix such as microporous fillers (e.g., carbon molecular sieves, zeolite) and nonporous nanoparticles (e.g., SiO_2, TiO_2). MMMs with microporous fillers could improve selectivity based on molecular sieving or surface flow transport mechanism, and it might also get an increased permeability if the preferred solid phase has a higher diffusion coefficient. While MMMs made by adding nonporous nanoparticles can improve gas permeability due to the increase of free volume. Chung et al. [25] reported that the properties for both polymer materials and inorganic fillers could affect the morphology and separation performance of MMMs. The rigid structure glassy polymers with high selectivity are more suitable for polymer matrix compared to rubbery polymers. However, the adhesion between glassy polymer phase and inorganic filler phase is a challenging issue for preparation of MMMs. Moreover, the thermal and chemical stabilities of MMMs are mainly dependent on physical property of a polymer matrix, which may suffer from the acid gases of SO_2 or NO_x that are usually involved in flue gas. MMMs normally present an enhanced mechanical strength compared to pure polymer membranes, and a reduced cost compared to pure inorganic membranes. However, the main challenge for preparation of

MMMs is to choose proper materials for both polymeric and inorganic phases to get a high gas separation performance and good compatibility. Examples for selection of polymer and inorganic filler for making CO_2 selective MMMs are reviewed in the literature [76, 149], and only the latest MMM materials are listed in Table 1. Recently, the PIMs/MOF MMMs with CO_2 permeance of 1740 GPU and enhanced selectivity (70%) and mechanical strength were reported by Ghalei et al. [44]; they concluded that membranes can be further optimized for economical CO_2 capture.

Carbon molecular sieve membranes

CMSMs are usually prepared by carbonization of polymeric precursors such as polyimide [10, 141, 142], polyacrylonitrile (PAN) [29], poly(phthalazinone ether sulfone ketone) [163], poly(phenylene oxide) [91, 161], and cellulose derivatives [65, 68, 72, 73, 90, 99]. CMSMs present high mechanical strength and moderate modulus due to their graphitic or turbostratic structure compared to graphitized fibers [130]. The separation mechanism of CMSMs is based on kinetic diameter difference in the gas molecules. CO_2 has a smaller kinetic diameter compared to O_2, N_2, and CH_4. The hollow fiber polyimide derived carbon membranes developed by Georgia Tech have been reported for different types of gas separations (e.g., CO_2/CH_4 and olefin/paraffin [134, 135, 155]). The issues related to high precursor cost and low gas permeance need to be further addressed. The cellulose acetate (CA)-based hollow fiber carbon membranes were developed by NTNU for biogas upgrading, natural gas sweetening, and H_2 separation [47, 53, 54, 97]. The main advantages of this type of carbon membrane are the low cost of CA precursor and the carbonization processability. However, it still has the challenges on (1) keeping deacetylated CA fibers straight during the drying process; (2) increasing gas permeance; and (3) reducing membrane aging due to the pore blockage of water vapor adsorption at relative humidity (RH) > 30%.

Although CMSMs present higher production cost, more challenges on module construction (due to the relatively brittle structures), and significant aging issue compared to most polymeric membranes, the advantages of high gas permeance and selectivity as well as high thermal and chemical stability still encouraged many researchers to develop carbon membranes for gas separation [68, 72, 88, 98, 141, 146, 161]. Considering the future commercial applications, strong effort should be put on the development of high performance asymmetric hollow fiber carbon membranes or tubular ceramic supported carbon membranes. Xu et al. prepared asymmetric hollow fiber carbon membranes for olefin/paraffin and ethylene/ethane separations [156, 157]. The PVDF-based asymmetric hollow fiber carbon membranes were reported for organic liquid separations [89].

Their investigation results showed a promising application of carbon membranes in energy-related processes. Recently, high flux ceramic supported carbon membranes with a high CO_2 permeance of 0.6 m^3(STP)/(m^2·h·bar) and CO_2/CH_4 selectivity of 30 were developed by Richter et al. [128], which can be potentially used for CO_2 removal from natural gas. However, the membrane cost and upscaling need to be further investigated.

CO_2 capture from power plant

The world fossil fuel power plants emit about two billion tons of CO_2 per year which should be significantly reduced according to the Kyoto protocol. CCS is one of the most promising options for the reduction of CO_2 emissions. Different techniques such as physical absorption (e.g., Selexol, Rectisol), chemical absorption (e.g., MEA, MDEA), physical adsorption (e.g., molecular sieves, metal organic frameworks), and gas separation membranes can be used to CO_2 capture from flue gas in power plants. Among them, amine absorption has been widely used in for CO_2 removal and considered to be the most mature technology. However, conventional amine absorption is an energy-intensive and high-cost process, which results in the large incremental costs of electricity generation. National Energy Technology Laboratory (NETL) estimated that amine unit will increase the cost of electricity production by 70% [38]. As an alternative, gas separation membranes and/or hybrid systems (e.g., membrane contactor, membrane-cryogenic process) for carbon capture, as illustrated in Fig. 2 [73], may have potentials to bring down the CO_2 capture cost in this application.

Gas separation membrane system

Yang et al. reviewed the progress of CO_2 separation using membrane technology, and they concluded that membrane process is energy-saving, space-saving, easy to scale-up, and can be a promising technology for CO_2 separation [158]. Strong effort has been put on the development of high-performance membranes (high CO_2 permeance and relatively good selectivities over other gas molecules) with good long-term stability for CO_2 capture, and some ultrathin nanocomposite and FSC membranes showed great potentials [16, 17, 50, 70, 77, 78, 107, 124, 139, 140, 158].

The Polaris® membranes developed by MTR has been demonstrated at pilot-scale for CO_2 capture from a natural gas combined cycle power plant [23]. A 20 ton/day skid was tested to validate the advanced modules (multi-tube and plate-and-frame) designed for low-pressure drop and small footprint, and the system showed quite stable performance over ca. 1000 h [106]. Moreover, MTR patented their process by feeding high CO_2 content air stream (air as sweep gas in the permeate side of the 2nd stage membrane unit) into the boiler to increase the CO_2 concentration in the flue gas [9], which can greatly reduce the required membrane area and energy consumption for this application.

It is worth noting that process design is crucial to improve the overall energy efficiency of the whole process with the integration of CO_2 capture unit. Many research work on technology feasibility analysis based on air sweeping process were reported. However, the influences of CO_2-contained air on the boiler operation should be further tested. It is worth noting that gas permeance of Polaris membranes has been significantly improved at lab-scale. Further pilot demonstration (field testing) is required to prove the performance at larger scale.

The large EU project NanoGLOWA (including 27 partners from European companies, universities, institutes and power plants) launched in 2006 was aiming at developing high-performance membranes for CO_2 capture from flue gas in post-combustion power plants. A small pilot-scale plate-and-frame module was installed in EDP's power plant in Sines (Portugal) to test the working of membranes in a real flue gas in 2011, and the membranes showed a stable performance over 6 months [52]. Recently, this type of membrane was
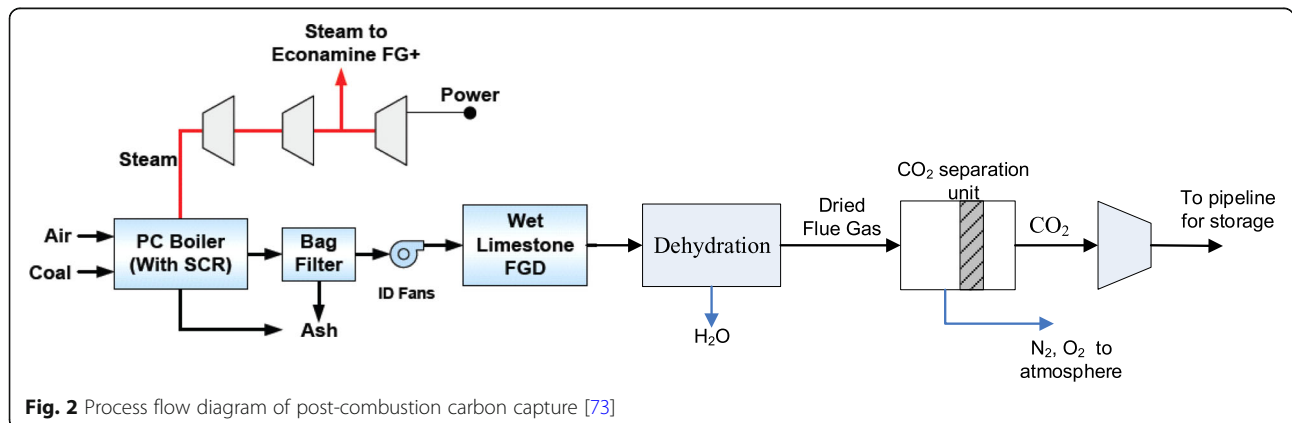
Fig. 2 Process flow diagram of post-combustion carbon capture [73]

demonstrated for CO_2 capture in the real flue gas from a propane burner at SINTEF Tiller plant (Trondheim, Norway) [74] and Norcem cement factory [51]. Two semi-commercial hollow fiber modules coated with PVAm selective layer (membrane area of 8.4 m^2) were performed in parallel in a single-stage process. The testing results indicated that a 60 vol% CO_2 purity was achieved in the permeate stream from a feed flue gas with 9.5 vol% CO_2 [74]. In December 2016, Air Products Ltd. licensed the PVAm-based FSC membranes for post-combustion CO_2 capture and will bring the technology to commercialization in the near future [48].

The PolyActive™ membranes developed by Helmholtz-Zentrum Geesthacht were tested for CO_2 capture from real flue gas using a pilot module with a membrane area of 12.5 m^2 [119]. The membrane system also showed stable performance over 740 h continuously, and they also reported that membrane processes was well suitable for post combustion CO_2 capture, and a CO_2 purity of 68.2 mol% in the permeate and a recovery of 42.7% can be achieved at the tested condition in a single-stage process. A two-stage pilot membrane system should be demonstrated to document the technology feasibility related to the energy consumption and the required membrane area. The engineering challenge on upscaling of envelop module needs to be addressed.

It should be remembered that techno-economic feasibility analysis should be conducted before bringing any type of membranes into commercial application. He et al. investigated the application of hollow fiber carbon membranes for CO_2 capture from flue gas [59]. They reported a capital cost of $100/tonne CO_2 avoided for carbon membrane system, which was higher than a traditional chemical method of MEA ($59/tonne CO_2 avoided reported by Rao and Rubin [125]), but the referred carbon membranes had a clear potential of further optimization. Merkel et al. [107] reported that membrane with a CO_2/N_2 selectivity above 50 and a CO_2 permeance of 4000 GPU could offer a capture cost below $15/tonne CO_2, which is lower than US Department of Energy's (DOE) target goal ($20/tonne CO_2). They also pointed out that improving membrane permeance is more important than increasing selectivity (if selectivity > 30) to further reduce the cost of CO_2 capture from flue gas [107]. He et al. [64, 70] and Hussain et al. [78] conducted process feasibility analysis by HYSYS integrated with an in-house membrane program (ChemBrane, developed by Grainger [46]) to investigate the influence of process parameters on energy demand and flue gas processing cost using a novel CO_2-selective FSC membrane. Their simulation results showed that membrane process using the high-performance FSC membranes was feasible for CO_2 capture to achieve > 90% CO_2 recovery and high CO_2 purity above 90%, even from a flue gas with a low CO_2 concentration (~ 10%). Ramasubramanian et al. reported a CO_2 capture cost of $25/tonne CO_2 using an

assumed membrane performance of CO_2 permeance of 3000 GPU (~ 8.2 m^3(STP)/(m^2 h bar)) and CO_2/N_2 selectivity of 140 [124]. More recently, membrane properties required for post-combustion carbon capture were systematically investigated [132, 133], and a permeance of at least 3 m^3(STP)/(m^2 h bar) with high selectivity should be achieved to be competitive to MEA absorption system. Even though the required high-performance membrane has not yet been achieved, their investigations emphasized quantitatively the need of improving the present membrane performance to realize a purely membrane-based process for CO_2 capture. Moreover, the CO_2 capture cost for membrane system is significantly dependent on the required CO_2 capture ratio. It is reported that membrane-based post-combustion CO_2 capture can benefit from lower CO_2 capture ratio with a 55% cost reduction [131], and CO_2 capture ratios lower than 90% would significantly improve the competitiveness of membrane-based carbon capture and lead to large cost reduction [132]. However, the overall benefit should be further investigated through the whole value chain. Therefore, the environmentally friendly technology with further improved membrane performance and properly selected process parameters and separation requirement (especially CO_2 capture ratio) can be a promising candidate for post-combustion CO_2 capture.

Gas-liquid membrane contactor

Membrane contactor combines the advantages of gas separation membrane technology with chemical absorption. In a membrane contactor, the membranes act as an interface between gas and liquid phase (solvent). For post-combustion CO_2 capture, CO_2 transports from the gas phase through microporous and hydrophobic membranes and is absorbed in the liquid phase. The CO_2-loaded liquids are then pumped to the desorber to release CO_2, while the regenerated solvents are recycled back to the membrane contactor [76]. This technology offers a unique way to perform gas-liquid absorption processes and provides a high operational flexibility [34]. Recently, strong interest has been focused on the efficiency studies of the membrane contactors for CO_2 capture [15, 24, 30, 34, 42, 94, 103, 121, 159]. Yeon et al. [159] reported the use of a PVDF hollow fiber membrane contactor for absorption and a stripper column as a desorber for CO_2/N_2 separation, which presented a higher CO_2 removal efficiency than the conventional absorption column. Chabanon et al. studied the wetting resistance of membrane contactors using different membrane materials, and they found that membrane contactors using composite hollow fiber membranes based on either a polymethylpentene (PMP) or a Teflon-AF thin dense layer coated on polypropylene (PP) supports showed remarkably stable performances over time compared to those of PP and polytetrafluoroethylene (PTFE) hollow fibers [24]. Feron et al. have investigated the potential application of CO_2 capture

from flues gas using a membrane contactor composed by porous polypropylene hollow fiber membranes and a dedicated absorption liquid (CORAL) [42]. Their results indicated that membrane contactor could be a promising candidate for CO_2 capture from flue gases in post-combustion power plants. Moreover, Dai et al. [27, 28] reported to use ionic liquid-based membrane contactor for pre-combustion CO_2 capture; the porous PTFE membrane and nonporous Teflon-PP (polypropylene) composite membranes were considered to be the most suitable membranes in this application. Even though the mass transfer resistance increases in membrane contactors particularly when membranes are wetted, the numerous advantages such as significantly increased interfacial area can potentially offset the disadvantages and makes membrane contactors to be promising in CO_2 capture [165].

CO_2 capture from industry

CO_2 emissions from industrial sectors such as steel/iron production, cement factory, and gas production plants contribute more than 10% of total CO_2 emissions. CO_2 removal from natural gas and biogas is mandatory to increase methane purity and avoid pipeline corrosion. Moreover, CCS is the only solution to reduce CO_2 emissions from cement factory as 50% of CO_2 is the by-product of a cement production process. Thus, CO_2 capture from those energy-intensive industries should also be implemented.

CO_2 removal from natural gas

Natural gas (NG) is becoming one of the most attractive growing fuels for world primary energy consumption due to its availability and versatility. NG is a less carbon-intensive and cleaner energy source compared to the other fossil fuels of coal and crude oil. However, raw natural gas in reservoirs or/and wells usually contains considerable amount of light and heavy hydrocarbons (HHCs), as well as the impurities such as water, H_2S, CO_2, N_2, and helium. Natural gas sweetening is mandatory in any natural gas plants to remove the acid gases of H_2S and CO_2 to meet the legal requirements and gas grid specifications. Different technologies such as chemical absorption [83], pressure swing adsorption (PSA) [81, 143], and membranes [2, 12, 43, 62, 63, 66–69, 93, 96] have been reported for CO_2 removal from natural gas. Decision on which technology used for CO_2 removal from natural gas is mainly dependent on process conditions and the raw natural gas composition. Conventional chemical (amine) absorption is well known and implemented in industrial processes, and still considered as the state-of-the-art technology for CO_2 capture. However, membrane systems possess many advantages such as small footprint, low capital, and operating costs are environmentally friendly and exhibit their process flexibility [11], which show a great potential for natural gas sweetening even though it has only a 5% of the market today.

Commercial membranes for natural gas sweetening are usually made from cellulose acetate and polyimide and have a typical CO_2/CH_4 selectivity of 15~30 [13]. Membrane systems are preferred for high CO_2 concentration gas streams (enhanced gas recovery plant, ca. 50% CO_2, and high pressure), and amine units are preferred for relatively low-concentration gas streams. Moreover, membrane systems are also favorable to be used for processing small gas flows because of their simple flow schemes (typically in offshore platforms, < 6000 Nm^3/h), while amine units are more complex and require careful, well-monitored operating procedures, as documented by Baker et al. [8]. Although common polymer membranes for natural gas sweetening are still cellulose acetate/triacetate and polyimide, the novel, high-performance FSC membranes and carbon membranes showed nice potentials for CO_2/CH_4 separation [32, 33, 55, 69].

High-pressure operation is one of the most challenging issues related to natural gas sweetening with membrane systems since membrane plasticization and compaction are found to be a well-known phenomenon in most polymer membranes [40, 152]. For the FSC membranes, carrier saturation at a high CO_2 concentration or partial pressure will additionally cause the reductions of CO_2 permeance and CO_2/CH_4 selectivity. The potential strategies to overcome membrane plasticization are cross-linking of membrane material [153] and fabrication of mechanical strong membranes with enhanced properties, e.g., mixed matrix membrane by adding inorganic fillers into the polymer matrix. Adams et al. prepared a 50% (vol.) Zeolite 4A/poly (vinyl acetate) MMM with increase separation performance for CO_2/CH_4 separation [2]. Their results showed a promising application for high-pressure natural gas sweetening. He et al. reported that CNTs reinforced PVAm/PVA blend FSC membrane presented a good CO_2/CH_4 separation performance at high pressure up to 40 bar [62, 63, 67–69], which showed a nice potential application for CO_2 removal from natural gas. There are, however, still challenges to maintain the separation performance at higher pressure > 40 bar (especially > 80 bar in subsea process), which can be potentially addressed by employing high-performance (to exceed the Robeson CO_2/CH_4 upper bound) carbon membranes with high mechanical strength to tolerate high pressure without losing separation performance.

Membrane system design for CO_2 removal from natural gas is mainly dependent on membrane performance, CO_2 concentration in feed stream, specific separation requirement, as well as plant location. Peters et al. conducted process design, simulation, and optimization for CO_2 removal from natural gas using HYSYS integrated with an in-house membrane program (ChemBrane) [118]. They reported that a two-stage membrane system

with a CO_2 permeance of 0.3 $m^3(STP)/(m^2$ h bar) and a CO_2/CH_4 selectivity of 40 is comparable to that of amine process [118]. Although the purity of sweet gas with membrane system is a little low, it can still achieve the sales gas standards (< 2% CO_2 in natural gas). It was also reported that two-stage membrane systems with a membrane unit cost < $60/m^2$ membrane area was viable for CO_2 removal from a CO_2 content (10 vol%) natural gas [66]. Moreover, membrane system presents a small footprint and flexibility, and is easy to maintain, which is crucial for subsea and offshore natural gas production. It should be noted that membranes for natural gas sweetening is one of the most promising application related to the market and economic benefit.

CO_2 removal from biogas

Biogas is usually produced from anaerobic digestion of wastes such as sewage sludge, animal manure, and organic fraction of household, which is mainly composed of methane (CH_4) and carbon dioxide (CO_2) and may also contain VOCs, H_2O, H_2S, and NH_3. Biogas has a potential of high energy due to the presence of high purity methane. However, depending on the end usage, a specific biogas treatment (i.e., biogas upgrading, defined as CO_2 removal from raw biogas) should be conducted to increase the calorific value of biogas. Therefore, it is crucial to identify energy-efficient technology for CO_2 removal from biogas at a low CH_4 loss. The common techniques for biogas upgrading include water scrubbing, PSA, chemical absorption (e.g., amines), and gas separation membranes. The selection of suitable technology is mainly dependent on plant condition, such as the availability of low price of thermal energy, electricity and water, as well as the plant capacity. In the European region, water scrubbing is the most prevailing technology at biogas plants (40%), and membrane has 4% of the market today [113]. Most biogas plants in Sweden are using PSA even though CH_4 loss is high (3–10%). The biogas plants using water scrubbing technology can get high purity CH_4 (> 99 vol%), but also produces a lot of wastewater and has high power demands. The amine scrubbing technology presents high selectivity to produce high purity methane, but the process is energy-intensive and environmentally unfriendly due to the needs of organic solvents of amines. Comparing to other state-of-the-art technologies, gas separation membrane processes present more energy- and space-saving and lower environmental impacts and are preferable for small-scale biogas plants < 1000 $m^3(STP)/h$ [108]. The commercial SEPURAN® membranes developed by EVO-NIK for biogas upgrading have low-energy requirements and low maintenance costs. The main challenge is to get high CH_4 purity and low CH_4 loss simultaneously. The latest reported single-stage polyimide membrane system

can only reach CH_4 purity of 80.7 vol% with a high CH_4 loss of 24%, which is unacceptable in any biogas production plants [111]. Using a multi-stage membrane system in series can get high purity CH_4, but CH_4 loss will be higher. A CH_4 loss to atmosphere of more than 4% leads to a non-sustainable process according to carbon footprint life cycle assessment[126], which is negative related to economy and environment impact due to the high global warming potential (GWP) of methane. Therefore, seeking a high CO_2/CH_4 selective membrane (at least > 30) is crucial to reduce CH_4 loss, simplify process design, and reduce energy consumption. The cellulose-derived hollow fiber carbon membranes have been reported for CO_2/CH_4 separation and presented a high CO_2/CH_4 selectivity over 100 [53, 72], which showed the potential for CO_2 removal from biogas. The techno-economic feasibility analysis also proved that carbon membrane can be a competitive technology for biogas upgrading compared to amine absorption [60]. Moreover, several carbon membrane modules (each one has the area of 2 m^2) were exposed to a real biogas (63 vol% CH_4, 1 ppm H_2S, balance CO_2) over 200 days at a biogas plant in Southern Norway. The biogas with 10 Nm³/h was fed into these modules at 20 bar. A high purity methane of 96 vol% and a CH_4 recovery of 98% was achieved [56], and the membranes showed stable performance over the testing period, which is considered at TRL 5. Although the reported pilot system can produce high purity biomethane as vehicle fuels, there are still challenges related to uniform packing of hollow fiber carbon membranes. Moreover, the brittleness of hollow fibers remained a challenge for module upscaling. Future researches should focus on improving mechanical properties and gas permeance, which directs to the development of asymmetric flexible hollow fiber carbon membranes or supported carbon membranes.

CO_2 capture from cement factory

Cement factory is pursuing solutions for carbon capture from high CO_2 content flue gas (ca. 17 vol% wet base) as it represents 7% of global anthropogenic CO_2 emissions. Application of CO_2 capture in cement kilns would have great potential to reduce CO_2 emission from these industries but will naturally influence cement production cost. Thus, the European cement industry (through HeidelbergCement) is taking big interest in low-cost CO_2 capture technologies.

Cement factory releases greenhouse gas emissions both directly and indirectly: limestone calcination directly releases ~ 50% of all CO_2 emissions in the cement production, while the burning of fuels to heat the kiln indirectly contributes another 50% CO_2 emissions. Employment of CCS is considered as one of the most important techniques to achieve the Norcem Zero CO_2 Emission Vision 2030. Three different technologies (amine absorption,

membranes, solid adsorbent) were tested on site to document the process feasibility [14]. There, the first pilot-scale membrane system using PVAm-based flat-sheet FSC membranes was tested for CO_2 capture from a 17 vol% (wet base) CO_2 flue gas in cement factory. Although many challenges related to process and module design were revealed, and it was also difficult to achieve a stable operation of membrane system, a CO_2 purity up to 72% was achieved for short periods when all process parameters were well controlled in the single-stage FSC membrane system [49]. The membrane efficiency of the plate-and-frame module was quite low, and the designed system suffered significant water condensation/corrosion issues. Thus, the hollow fiber FSC membrane modules with total membrane area of ca. 20 m^2 were constructed by the joint force from Air Products and Chemicals, Inc., in 2016 [51]. In that project, the pilot FSC membrane system was evaluated at TRL 5. The system was tested over 6 months at different conditions, and stable performance was found even at a high NO_x and SO_2 loading (average 100 ppm and 5 ppm, respectively) flue gas. They reported that stable permeate CO_2 purity of 65% over the accumulated 24 days was achieved. The techno-economic feasibility analysis was also reported to achieve 80% CO_2 recovery and > 90% CO_2 purity. However, the designed two-stage membrane system was difficult to achieve specific CO_2 purity (> 95%) requirement (especially the low O_2 limitation) for enhanced oil/gas recovery (EOR/EGR). The potential solutions are to introduce a third-stage membrane unit or a low-temperature liquefaction unit. It should also be remembered that proper pre-treatment processes (e.g., particle filtering, water condensation) are always required to protect membrane system for CO_2 capture in cement factory.

CO_2 capture from iron/steel making industry

Recently, CO_2 capture from power generation has received a lot of attention as described in the section "CO2 capture from power plant". However, only a few studies reported on CO_2 capture in iron/steel manufacture industries [39, 45, 100, 150]. The previous large European projects, Ultra Low CO_2 Steelmaking (ULCOS) focused on the development of new steel production technology that could drastically cut CO_2 emissions to 50% by the year 2030 (base year 2004), and membrane system was chosen for investigation of CO_2 capture from nitrogen free blast furnace (NFBF) exhaust gases (N_2/CO_2/CO/H_2: 10%/36%/47%/7%). Lie et al. reported that PVAm/PVA blend FSC membranes can become a potential candidate for CO_2 capture from flue gas in steelmaking industry with 15.0–17.5 €/tonnes CO_2 [100]. Recently, Roussanaly et al. reported on the simulation of different membranes for CO_2 capture from steel industry with a 30% CO_2 in feed gas, and a relatively low CO_2 capture cost was identified compared to carbon capture in other processes [131]. However, it should be noted that the feed gas only contains CO_2 and N_2 in their study, while CO, H_2 are neglected which usually existed. Thus, further investigation with more accurate feed gas composition should be conducted to document the economic feasibility.

Future perspectives

The deployment of CO_2 capture in power plants and process industries is crucial to reduce CO_2 emissions, and several technologies should be alternatively employed depending on flue gas composition, plant location, and separation requirement. Amine absorption is still considered as the most mature technology today for large- or full-scale applications and developing next generation advanced solvents should be pursued to reduce energy consumption. Gas separation membranes, especially ultrathin polymeric and FSC membranes, for post-combustion CO_2 capture were demonstrated at pilot-scale with stable performance over long-term period and considered as the most technology regarding to the environmental impact and energy efficiency. However, membrane performance should be further improved to reduce CO_2 capture cost down to $20/tonne CO_2. Moreover, process design need to be carefully considered to make a right choice, and a two/multi-stage system is usually required to achieve high CO_2 capture ratio and CO_2 purity simultaneously. Nevertheless, membrane systems, which require no chemicals, are easy to scale up and have a relatively low-energy demand and could be an environmentally friendly technology for CO_2 capture from power plants and other energy-intensive process industries in the future.

Availability of data and materials
Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

Author's contribution
The author wrote, read, and approved the final manuscript.

Competing interests
The author declares that he has no competing interests.

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