Status and progress of membrane contactors in post-combustion carbon capture: A state-of-the-art review of new developments

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ABSTRACT

Post-combustion carbon capture (PCC), which can be retrofitted to existing units in power plants worldwide, is regarded as the first technologically feasible and effective way to combat human-induced climate change. The membrane contactor is an emerging and promising membrane technology for PCC as it integrates the benefits of both liquid absorption (high selectivity) and membrane separation (modularity and compactness). This review aims to provide a state-of-the-art assessment of the research work carried out so far on membrane contactor technology in PCC. It details common aspects of membrane contactors, such as technological advantages, membrane wetting, mass transfer and module design, as well as new advances (e.g., new membranes and absorbents used in absorption processes) and novel applications (e.g., direct CO_2 stripping and integrated heat recovery in desorption processes). Moreover, the difference in performance between membrane absorption and conventional absorption is also compared and discussed. Lastly, we discuss the status and progress of membrane contactors in PCC and offer some recommendations for future work. This paper provides a clear overview on the recent developments of membrane contactor technology in PCC.

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Contents

1. Introduction

Carbon dioxide (CO_2) is the major greenhouse gas contributing to global climate change. CO_2 concentrations in the atmosphere have increased by more than 100 ppm since their pre-industrial levels ($\sim$280 ppm), reaching 384 ppm in 2007 [1–3]. Worldwide, fossil fuel-fired power plants are the largest point sources of CO_2 emissions [4]. Therefore, CO_2 capture from power stations is of great importance in addressing the global concern of climate change.

1.1. Post-combustion carbon capture

Currently, there are three widely studied technologies for carbon capture: pre-combustion capture, post-combustion capture (PCC) and oxy-fuel combustion. Of these, PCC holds the greatest promise because it can be retrofitted to existing units in power plants.

However, there are several challenges in capturing CO_2 from flue gas because of its special properties (Table 1). These include low flue gas pressure ($\sim$1 atm), low CO_2 concentration in the flue gas (typically < 16%), and small size difference among the gas molecules. All these factors reduce the effectiveness of current separation technologies and increase costs [5].

Liquid absorbent based PCC is recognized as the state-of-the-art carbon reduction technology, to a large extent due to its high CO_2 removal efficiency (usually > 80%) from flue gas even at low CO_2 concentrations [6,7]. A typical liquid absorbent based PCC system is illustrated in Fig. 1. The flue gas from the power plant undergoes pretreatment and cooling before entering the absorber. Pretreatment aims to remove undesirable particles, SO_x and NO_x that adversely affect CO_2 absorption. The flue gas temperature should be cooled to 45–50 °C to minimize evaporated solvent loss

and maximize CO_2 absorption [2]. The cooled flue gas is absorbed by the solvent in the absorber, forming CO_2 rich solvent. The scrubbed gas, along with a small amount of solvent is then water washed and vented to the atmosphere. The CO_2 rich solvent is preheated via a lean/rich heat exchanger by the regenerated CO_2 lean solvent, and then pumped to the top of the desorber. CO_2 is thermally released in the desorber where substantial amounts of thermal energy are supplied via the reboiler.

Currently, amine-based absorption is the leading technology for CO_2 capture, which occupies more than 90% of the market. In a conventional absorption plant, acid gas is brought in direct contact with lean solvent inside an absorber (usually a high column), where mass transfer takes place at the gas–liquid interface [8]. As absorption of CO_2 in a liquid is a process with equilibrium limitation, vapor-liquid equilibrium, operating conditions, physiochemical properties, and reaction equilibrium and kinetics play important roles in determining the required interfacial areas, and thus the height of an equilibrium stage and the design of the

Table 1
Typical properties of coal-fired flue gas after SO_2 scrubbing in post-combustion carbon capture (modified from [5,233]).

Flue gas	Composition or condition	Kinetic diameter (Å)
CO_2	10–16 wt%	3.30
N_2	70–75 wt%	3.64
H_2O (vapor)	5–7 wt%	2.65
O_2	3–4 wt%	3.45
CO	$\sim$20 ppm	3.75
NO_x	< 400 ppm	
SO_x	< 400 ppm	
Temperature	45–120 °C	
Pressure	$\sim$ 1 bar	

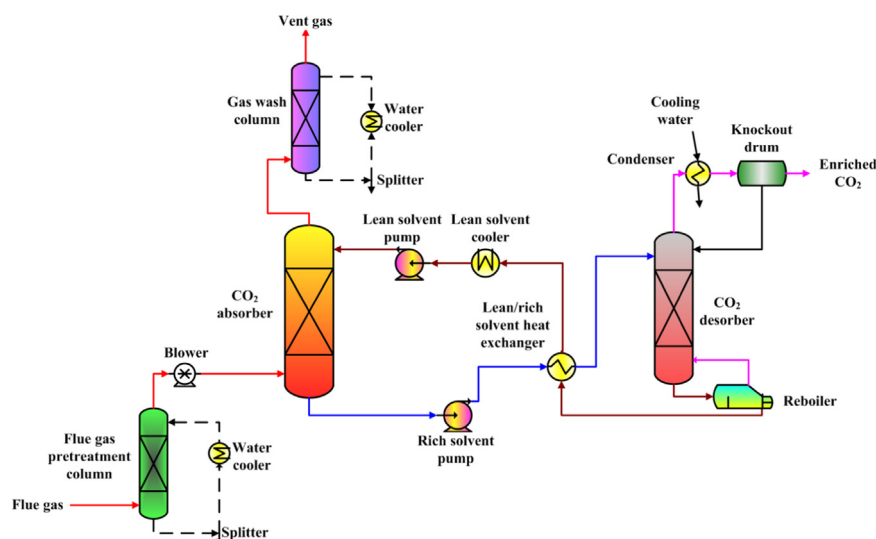Note: the water vapor content is dependent upon the flue gas temperature.

Fig. 1. Typical process configuration of a liquid absorbent based post-combustion carbon capture process.

contacting equipment. Current industrial absorbers (gas–liquid contactors) can be classified into two main categories [9]:

i. *Differential gas–liquid contactors*: including packed columns, bubble columns and spray towers, where mass transfer happens within the entire length of the contactor and gas–liquid equilibrium is not reached in any point of the equipment.

ii. *Stage-wise gas–liquid contactors*: such as plate columns and rotating disc contactors, in which gas–liquid equilibrium is reached within each stage of the equipment, thus mass transfer happens only in a part of the volume at each stage.

In particular, the gas–liquid interfacial area and the liquid holdup are important factors in contactor design [9]. Usually, a low value of liquid holdup in a gas–liquid contactor is not optimal due to the economy of the process, as a large contactor is then required. However, if the interfacial area of the contactor is high, then low liquid holdup becomes an advantage, because it enables the use of more costly absorbents (e.g., ionic liquids and enzyme-based absorbents).

Although liquid absorbent based PCC is a relatively efficient and mature technology for carbon capture, it still faces some crucial problems. These include its sizeable energy consumption, large footprint, equipment corrosion, foaming and solvent loss through degradation and by entrainment. Membrane contactor technology is a promising alternative that could overcome these problems [10–13].

1.2. Membrane contactors

Membrane contactor technology for gas absorption is also well-known as membrane (gas) absorption. Membrane contactors have attracted considerable research interest since the 1980s, with Qi and Cussler being the first to use hollow fiber membrane contactors for CO_2 absorption [14,15]. In practice, membrane contactors can capture CO_2 as well as other gases/vapors, such as SO_2 [16], H_2S [17] and volatile organic compounds (VOCs) [18]. Membrane contactors have also been successfully commercialized in a number of gas–liquid applications, such as CO_2 and O_2 removal in beer production, production of ultrapure water in the semiconductor industry, and membrane distillation [10].

Compared with conventional absorption systems, membrane contactors have significant advantages [10,19–21]. The advantages and disadvantages of membrane contactors in gas absorption are summarized in Fig. 2. Membrane contactors are non-dispersive contacting systems in which the membranes do not provide selectivity for separation but instead act as barriers to separate two phases and increase the effective contact area for mass transfer. One of the most noticeable advantages of membrane contactors is their extremely high interfacial area, which can significantly reduce equipment size and thus lead to process intensification [15,19,22–24]. Membrane contactors can offer around 30 times more interfacial area than conventional gas absorbers [10], and they could reduce absorber size by 10-fold [25,26].

Falk-Pedersen et al. [23] reported a CO_2 removal membrane contactor unit for the absorption of exhaust gas from a LM 2500+ gas turbine on an offshore installation, which provides a good example of the advantages. The absorbent employed is the conventional aqueous amine solution containing 30 wt% mono-ethanolamine (MEA). The use of membrane contactors in the same process eliminated or significantly reduced many operating problems, such as foaming and corrosion. Several benefits have been quantified [23], including

- operating cost savings of 38–42%;
- dry equipment weight reduction of 32–37%;
- operating equipment weight reduction of 34–40%;
- total dry weight reduction of 44–47%;
- total operating weight reduction of 44–50%;
- footprint requirement reduced by 40–50%;
- capital cost reduction of 35–40%.

The advantages of membrane contactors are principally attributed to integration of the benefits of both liquid absorption (high selectivity) and membrane separation (modularity and compactness) [10,27]. The major disadvantage of membrane contactors is the increased mass transfer resistance, particularly when membranes are wetted. Nevertheless, reduced mass transfer coefficients can be outweighed by the numerous advantages (e.g. significantly increased interfacial area), which makes membrane contactors strongly competitive with conventional systems in CO_2 capture.

1.3. Aim and novelty of this paper

This paper aims to provide a state-of-the-art assessment of research work carried out to date on membrane contactor
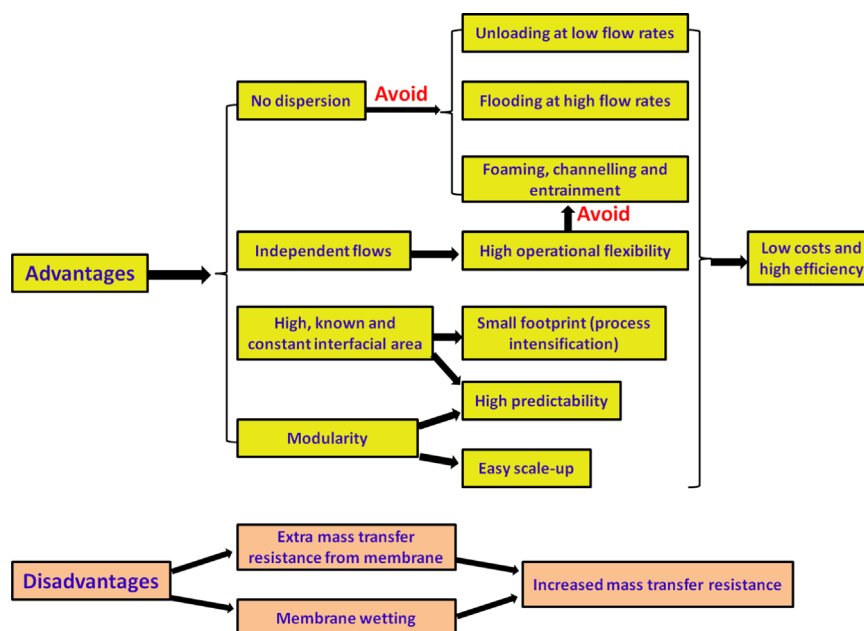
Fig. 2. Summary of the advantages and disadvantages of membrane contactors in gas absorption.

technology in PCC, starting with a brief overview of pilot plant demonstrations. We revisit the frequently mentioned challenges, such as membrane wetting, mass transfer and module design in previous relevant review papers [19–21]. We also compare the performance difference between membrane absorption and conventional absorption, and detail new developments (e.g., on new membranes and absorbents used in absorption processes) and novel applications (e.g., for both direct CO_2 stripping and integrated heat recovery in desorption processes) of membrane contactors.

2. Major PCC pilot plant demonstrations with membrane contactors

2.1. Early trials by Kværner Process Systems (KPS) in Norway

Over 20 years ago, motivated by the introduction of a North Sea carbon tax ($\sim$US \$53/tonne CO_2) in 1991, for the first time KPS initiated a joint program of developing membrane contactor technology for CO_2 capture in 1992 [28,29]. W.L. Gore & Associates GmbH (GORE) provided polytetrafluoroethylene (PTFE) membranes, SGL Carbon Group (SGL) made the modules and Ottestad Breathing Systems (OBS) made the membrane protection system. The first application of interest was the removal of CO_2 from gas turbines on off-shore oil and gas platforms, where conventional gas–liquid contactor technology was too bulky and heavy to be applied. Membrane contactor technology provided the opportunity for size and weight reductions which would enable the capture and storage of CO_2, thus avoiding the tax on these emissions.

Membrane contactor performance tests were started in 1995. Large scale pilot trials were performed between 1998 and 2001 for a total of 7000 h with 8 membrane modules ($\sim$5000 h for the longest running time with one module) [23]. The exhaust gas flow rate was 2610 kg/h and the membrane contactor showed a CO_2 capture efficiency of 85% (195 kg/h) without decline in membrane performance. The project demonstrated that membrane contactor technology was the best alternative to conventional absorption columns, with significant reduction in size, weight, operating and capital costs [23,29]. Further work was carried out using the MHI KS-1 solvent at the Nanko PCC pilot plant operated by Kansai

Electric in Japan, which was supported by the CO_2 Capture Project (CCP), global partnership of mainly oil and gas companies [30]. Performance in the pilot plant was validated by a dedicated process model and this enabled scale-up studies, showing an 8-fold size reduction in absorber size, and a 5-fold reduction in weight compared to a conventional packed column. Despite these massive technical improvements, capital costs were reduced by only 9% and operation costs by nearly 30%, the latter reduction most likely due to the use of an improved absorption liquid, KS-1 solvent. KPS also initiated a significant development program in natural gas treatment, which not only covered CO_2 but also H_2S removal and dehydration applications.

Despite the apparently successful demonstration projects, the technology did not reach commercial status. While the underlying reasons have not been clarified, it appears that the technical advantages of the membrane contactor technology did not fully translate into overall cost reductions for the applications considered. Moreover, for the application that the membrane contactor technology was originally proposed, i.e. reduction of off-shore, taxed CO_2-emissions, increasingly the electricity requirements of the oil and gas platforms have been met by supply from on-shore power generation which has a very low carbon intensity in Norway.

In similar time periods, researchers in Japan also employed PTFE membrane contactors with a 5 M MEA solution as the absorbent for CO_2 capture. It was confirmed that the PTFE membrane was stable during long-term operation ($>$6600 h) and that the overall volumetric mass transfer coefficient of the membrane contactor was more than 5 times larger than of the a conventional packed bed [31]. The early pilot scale experiments proved that membrane contactor technology with robust membranes is promising for CO_2 capture.

2.2. Early pilot plant development work at the Netherlands Organization for Applied Scientific Research (TNO)

Throughout the 1990s, TNO conducted an extensive program of membrane contactor development. The program involved a large number of applications, including separation of CO_2 from different source streams [32]. Building on successful early trials for SO_2 removal from flue gases [33], TNO established a pilot plant for CO_2

capture from flue gases from a gas-fired power station in the Netherlands in 1997 [25]. The CO_2 capture trials used an aqueous amino-acid salt solution as the liquid absorbent that was developed to avoid wetting of the porous polypropylene membranes used. TNO selected this type of membrane because of its low costs and its large production base derived from medical applications. This was an important technology attribute for the achievement of lower cost technology compared to conventional packed columns. The technological development was aimed at the provision of CO_2 to greenhouses with the aim of promoting plant growth and hence increasing horticultural productivity at reduced costs. This is common practice in the Netherlands with CO_2 provided by industrial gas companies or through the combustion of natural gas. Apart from the cost prerogative, the CO_2 quality was an important performance determining factor and the pilot plant trials were primarily aimed at assessing the CO_2-quality from the membrane contactor and amino-acid salt based technology. In addition to the dedicated liquid absorbent development, TNO also focused its efforts on the development of a transversal flow membrane module, which was considered to be beneficial for scale-up and mass transfer optimization [33,34]. The CO_2 development program incorporated a series of niche applications such as CO_2 removal from enclosed spaces such as submarines [35]. Although the technology commercialization was not successful in the 1990s, TNO maintains activities in the membrane contactor domain.

2.3. Trials by the Cooperative Research Center for Greenhouse Gas Technologies (CO2CRC) in Australia

Australia relies heavily on coal resources for its power, emitting considerable amounts of greenhouse gases. To reduce CO_2 emission, the government initiated a fund under the Energy Technology Innovation Strategy (ETIS), and established the CO2CRC in 2003 [36]. In 2009, researchers from the CO2CRC started CO_2 absorption trials with three types of membrane contactors, including porous polypropylene (PP), porous PTFE and non-porous polydimethylsiloxane (PDMS). An amino acid based commercial solvent PuraTreat™ F was used as the liquid absorbent. It was found that the PP membrane contactor suffered from severe pore wetting, the PTFE contactor experienced minor wetting, and the nonporous PDMS contactor was free of wetting but had two orders of magnitude lower mass transfer coefficient that the PP membrane contactor [37]. It does not appear that these trials had a commercialization follow-up.

2.4. Recent trials by Gas Technology Institute (GTI) in the United States (US)

Since 2010, the US Department of Energy (DOE) has funded GTI to develop the membrane contactor technology for CO_2 capture with new polyether ether ketone (PEEK) membrane materials provided by the PoroGen Corporation [38]. The PEEK membrane contactor has excellent thermal and chemical stabilities, ensuring high absorption performance. The membrane absorption technology is called Carbo-Lock™, which can be used for cost-effective separation and capture of CO_2 from various emission sources. GTI has considerable experience in membrane contactor technology development through its collaboration with KPS in the 1990s.

Activated methyldiethanolamine (aMDEA) and activated K_2CO_3 solvents were respectively used as the absorbent in the test for ~120 h. CO_2 capture efficiency was always higher than 90% with 95% CO_2 purity even in single stage trial [39]. It was also demonstrated that the measured volumetric mass transfer coefficient of the membrane contactor was more than 20 times higher than that of a conventional packed column and that gas contaminants (including O_2, NO_2 and SO_2) had insignificant effects on CO_2 capture

performance [39,40]. The CO_2 capture cost was ~US $55/tonne CO_2 when using aMDEA as the solvent at a membrane cost of $30/$m^2$. The capture cost could be further reduced to reach the DOE's goal in 2025 ($40/tonne CO_2) by decreasing membrane module cost and using advanced solvents [40].

2.5. Evaluation from membrane contactor pilot plant results

The pilot plant projects discussed in the previous section have demonstrated that despite ongoing concerns around membrane wetting, the technology can operate in actual gas treatment applications. The three main approaches to membrane wetting, i.e. maximization of hydrophobicity of the membrane, use of high surface tension liquid absorbents with negligible vapor pressure and use of non-porous high-flux membranes have all been successfully demonstrated in pilot plant projects. Some of these approaches might reduce the benefit of mass transfer intensification and the subsequent potential for reduction of the equipment footprint. The resulting benefit of these improvements of the membrane contactor technology robustness will most likely outweigh a loss in mass transfer efficiency and enable commercial deployment. Such benefits need to be confirmed in continued pilot plant experiments incorporating long-term evaluation of the technology.

In all large-scale demonstrations with membrane contactors, wetting is still a problematic concern, which limits the selections of membrane materials and absorbents. Inexpensive but robust membrane materials, less corrosive and environmentally friendly absorbents, and smart selection of membrane-solvent combinations are of great significance in future studies. It is worth noting that new systems/devices may be required to carefully control gas pressure drops and fluctuations, particularly for carbon capture from gas plants where gas pressure is much higher than the pressure of flue gas in coal-fired power plants [41,42]. Controlling gas pressure drops and fluctuations along and across the membrane might be very challenging in long-term operations. Failure to control differential pressures may cause critical wetting problems.

Although membrane contactors for CO_2 capture have been proposed for more than three decades [14,15], it appears that commercial applications of this technology are still lacking, possibly due to the following limitations:

- The membrane brings an extra mass transfer resistance to the process, which becomes particularly severe when the pores of the microporous membranes become wetted.
- Transmembrane pressure must be precisely controlled when a microporous membrane is used in the contactor, otherwise the pore-wetting and even flow of fluids across the membrane (breakthrough) will occur.
- The lack of long-term stability or poor compatibility of the membrane and sealing materials with some organic solvents may limit the life time of the membrane module. Periodic replacement of membranes may incur a substantial extra cost.

3. Membrane contactors for CO_2 absorption

The use of membrane contactors for CO_2 absorption has continued to be a research focus in recent years [43]. The relevant studies can be categorized into the following groups: mass transfer and simulation, membrane wetting, membrane development, absorbent selection, and module design.

3.1. Mass transfer fundamentals

In a membrane contactor, gas and liquid phases are separated by porous membranes. Mass transfer through the porous membrane is illustrated in Fig. 3. It generally includes three consecutive steps: (i) diffusion from the bulk gas to the gas-membrane interface, (ii) diffusion through the membrane pores from the gas-membrane interface to the liquid-membrane interface, and (iii) transfer from the liquid-membrane interface to the bulk liquid followed by physical and/or chemical absorption. This is well known as the resistance-in-series model (Fig. 3).

Fig. 3A shows the mass transfer through a porous membrane in the non-wetted mode, which is more widely studied and preferred than the wetted mode. Gas flux (N) for the three regions (i.e., gas, membrane and liquid) can be expressed by:

$$N = k_g\left(P_{gb} - P_{gm}\right) = k_m\left(P_{gm} - P_{lm}\right) = k_l(C_{lm} - C_{lb}) \tag{1}$$

where k_g, k_m and k_l are the individual mass transfer coefficients for gas, membrane and liquid, respectively. P and C are the gas partial pressure and liquid concentration, respectively. The subscripts gb, gm, lm and lb represent gas bulk, gas-membrane interface, liquid-membrane interface and liquid bulk, respectively.

According to Henry's Law, the gas partial pressure above the liquid at equilibrium is related to the gas concentration dissolved in the liquid [44]:

$$P_{lm} = HC_{lm} \tag{2}$$

where H is the Henry's Law constant.

The overall mass transfer coefficient K_g based on the gas phase, and K_l based on the liquid phase can be written as

$$N = K_g\left(P_{gb} - P^*\right) = K_l(C^* - C_{lb}) \tag{3}$$

where

$$P^* = HC_{lb} \text{ and } P_{gb} = HC^* \tag{4}$$

Based on Eqs. (1)–(4), we obtain:

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{1}{k_m} + \frac{H}{k_l} \tag{5-A}$$

$$\frac{1}{K_l} = \frac{1}{HK_g} = \frac{1}{Hk_g} + \frac{1}{Hk_m} + \frac{1}{k_l} \tag{5-B}$$

In practical operations, a membrane contactor module might consist of a number of small hollow fibers where the tube wall thickness generally cannot be ignored. The mass transfer through a hollow fiber membrane is shown in Fig. 3C. Taking the membrane wall thickness into consideration, we obtain:

$$N = k_g\left(P_{gb} - P_{gm}\right)\left(\pi d_o L\right) = k_m\left(P_{gm} - P_{lm}\right)\left(\pi d_{ln} L\right)$$
$$= k_l(C_{lm} - C_{lb})\left(\pi d_i L\right) \tag{6}$$

$$N = K_g\left(P_{gb} - P^*\right)\left(\pi d_o L\right) = K_l\left(C^* - C_{lb}\right)\left(\pi d_i L\right) \tag{7}$$

where d_o, d_i and d_{ln} are the outer, inner and logarithmic mean diameters of the membrane, respectively.

The overall mass transfer coefficient K_g based on the gas phase, and K_l based on the liquid phase can be respectively expressed as:

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{d_o}{k_m d_{ln}} + \frac{Hd_o}{k_l d_i} \tag{8-A}$$
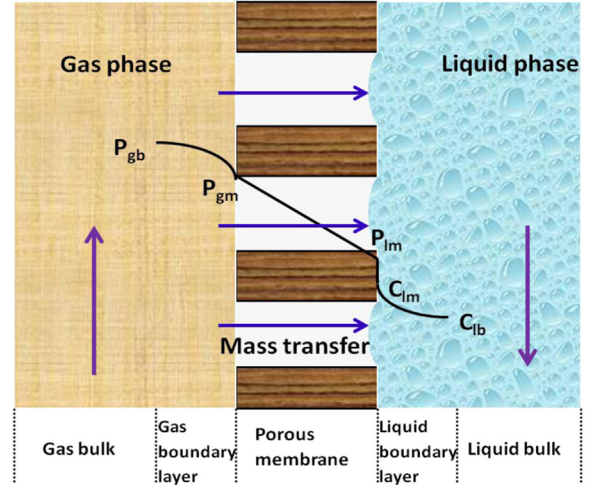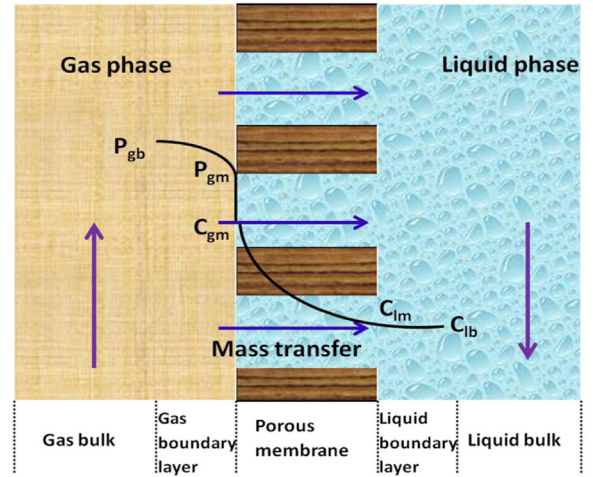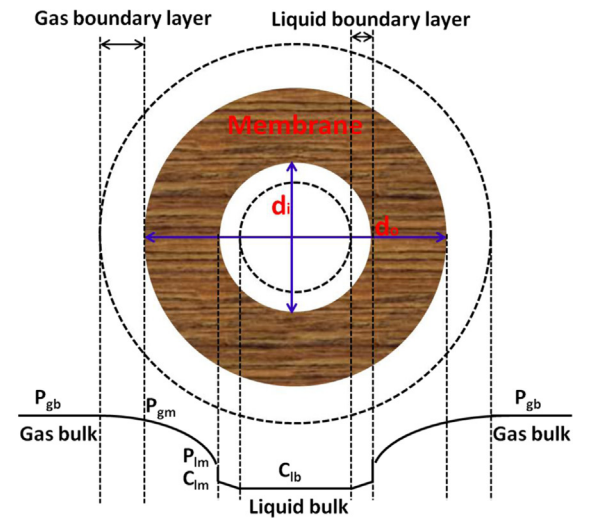
Fig. 3. Mass transfer mechanism through a porous membrane in (A) non-wetted mode (with gas filled pores); (B) wetted mode (with liquid filled pores); (C) through a hollow fiber (gas on the shell side and liquid on the tube side). P and C are the gas partial pressure and liquid concentration, respectively. The subscripts gb, gm, lm and lb represent gas bulk, gas-membrane interface, liquid-membrane interface and liquid bulk, respectively.

$$\frac{1}{K_l} = \frac{d_i}{Hd_oK_g} = \frac{d_i}{Hd_ok_g} + \frac{d_i}{Hd_{ln}k_m} + \frac{1}{k_l} \tag{8-B}$$

When considering the enhancement factor (E) due to chemical reaction, we obtain:

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{d_o}{k_md_{ln}} + \frac{Hd_o}{Ek_ld_i} \text{ (Liquid on the tube side)} \tag{9-A}$$

$$\frac{1}{K_l} = \frac{d_i}{Hd_oK_g} = \frac{d_i}{Hd_ok_g} + \frac{d_i}{Hd_{ln}k_m}$$
$$+ \frac{1}{Ek_l} \text{ (Liquid on the tube side)} \tag{9-B}$$

The above equations stand when the liquid phase is on the tube side without wetting (i.e. gas phase is on the shell side). If the liquid phase flows on the shell side (i.e. gas phase is on the tube side), then:

$$\frac{1}{K_g} = \frac{1}{d_ik_g} + \frac{1}{d_{ln}k_m} + \frac{H}{Ed_ok_l} \text{ (Gas on the tube side)} \tag{10-A}$$

$$\frac{1}{K_l} = \frac{d_o}{Hd_iK_g} = \frac{d_o}{Hd_i^2k_g} + \frac{d_o}{Hd_{ln}d_ik_m}$$
$$+ \frac{1}{Ed_ik_l} \text{ (Gas on the tube side)} \tag{10-B}$$

Some researchers [45] take a different format of Henry's Law in membrane processes, i.e., $C_{lm}=HP_{lm}$, obtaining

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{d_o}{d_{ln}k_m} + \frac{d_o}{EHd_ik_l} \text{ (Liquid on the tube side)} \tag{11-A}$$

$$\frac{1}{K_l} = \frac{Hd_i}{d_oK_g} = \frac{Hd_i}{d_ok_g} + \frac{Hd_i}{d_{ln}k_m} + \frac{1}{Ek_l} \text{ (Liquid on the tube side)} \tag{11-B}$$

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{d_i}{d_{ln}k_m} + \frac{d_i}{EHd_ok_l} \text{ (Gas on the tube side)} \tag{12-A}$$

$$\frac{1}{K_l} = \frac{Hd_o}{d_iK_g} = \frac{Hd_o}{d_ik_g} + \frac{Hd_o}{d_{ln}k_m} + \frac{1}{Ek_l} \text{ (Gas on the tube side)} \tag{12-B}$$

The mass transfer fundamental in membrane contactors can be well explained with the above equations. Eqs. (9)–(12) or their derivative formulae have been adopted in a number of studies [46–50]. However, because the format of Henry's Law used or the membrane-fluid orientation was not always clear in the literature, the equations were sometimes confusing. Eqs. (9)–(12) clarify the general mass transfer in membrane contactors under different flow orientations.

3.2. Major challenges for membranes

The main challenges faced when using membrane contactors include membrane wetting, fouling and degradation. These are discussed in detail below.

3.2.1. Membrane wetting

Wetting in membrane contactors is the most important challenge to overcome, because it can significantly increase the mass transfer resistance and thus lead to a sharp drop in absorption performance [51–55]. Rangwala [52] reports that membrane resistance can be up to 60% of the total mass transfer resistance when the membrane has marginal wetting (< 2%). Wang et al.

[56] observed that the CO_2 absorption in non-wetted mode is six times higher than that in wetted mode, and that the reduction in overall mass transfer coefficient can reach 20% even when the membranes are 5% wetted.

3.2.1.1. Fundamental of membrane wetting. For a liquid absorbent, its wettability to a membrane is generally evaluated via the liquid entry pressure (LEP, also called breakthrough pressure) [57,58]. LEP, defined as the minimum pressure applied on the liquid to enter the membrane pores, can be estimated by the Laplace-Young equation [59,60]

$$LEP = -\frac{4B\gamma\cos\theta}{d_{max}} \tag{13}$$

where B is the pore geometry coefficient ($B=1$ for perfectly cylindrical pores; $0 < B < 1$ for non-cylindrical pores), γ is the liquid surface tension, θ is the contact angle between the liquid absorbent and the membrane surface, and d_{max} is the maximum pore diameter of the membrane.

Once the LEP has been achieved, the largest pores become wetted first, followed by successively smaller pores until the membrane structure becomes completely wetted. Once all the pores are wetted then the solvent flow into the gas phase will follow Darcy's law, driven by the transmembrane pressure difference [61].

Recently, wetting phenomenon were comprehensively reviewed by Mosadegh-Sedghi [51]. Three modes of wetting in membrane contactors have been discussed [20,21,51,62]: (A) non-wetting mode, (B) complete-wetting mode and (C) partial-wetting mode. A membrane contactor with highly hydrophobic hollow fibers may undergo all three wetting patterns over prolonged operation. In the first few hours, the membrane module may be non-wetted (Fig. 3A) and thus have high absorption efficiency. After a few days, it may become gradually wetted (i.e., partially wetted), at which time the absorption efficiency reduces dramatically. Over a few months or years of operation, the membrane pores could be completed filled with the liquid absorbent (i.e., completely wetted, Fig. 3B). In real conditions, membrane pores are most likely to be partially filled with liquid absorbents (i.e., in partial-wetting mode).

Wetting is influenced by membrane characteristics (e.g., pore diameter, tortuosity, porosity and surface roughness), solvent properties (e.g., surface tension), the interaction between the solvent and the membrane (e.g., the liquid contact angle), and operating conditions (e.g., pressure on the liquid side).

3.2.1.2. Mechanisms of wetting. Membrane wetting has been explained by several different mechanisms. It is widely accepted that chemical reactions between the membrane and the absorbent in a membrane contactor will lead to membrane degradation and thus wetting. Wang et al. [56] observed that aqueous diethanolamine (DEA) solutions change the morphology of the membrane, suggesting that membrane degradation is caused by the chemical reaction between DEA and the membrane. Lv et al. [63] observed significant changes in membrane surface morphology, surface roughness and hydrophobicity after wetting, and claim that membrane wetting results from the absorption-swelling mechanism. Rangwala [52] report that ionic species and trace impurities in the absorbent can modify the membrane surface and allow liquid penetration into the pores by a necking phenomenon. Pore enlargement is also considered as the main reason for membrane wetting in chemical absorption [50].

Based on these explanations for membrane wetting, we envisage the following wetting process in most laboratory investigations:

i. Liquid absorbents contact the membrane surface at a contact angle above 90° (i.e., non-wetted).
ii. Liquid absorbents physically and/or chemically change the membrane surface properties (e.g., hydrophobicity, morphology, roughness and chemical compositions).
iii. Liquid absorbents penetrate into the pores and further change the pore properties, resulting in wetting.

In addition to direct water and/or absorbent penetration into the pores, wetting may be caused by capillary condensation of water vapor in the membrane pores [49]. Particularly, capillary condensation can be a real issue in membrane desorption, when there is a significant water vapor flow into the colder section of the fiber.

3.2.1.3. Prevention of wetting. To prevent pore wetting, the transmembrane pressure should be always maintained below the LEP. According to the Laplace-Young equation, LEP can be increased by employing absorbents with high surface tension, increasing the cosine of contact angle, and using membranes with small pore size. Li and Chen [19], and Mosadegh-Sedghi et al. [51] summarized several more specific measures for wetting prevention:

i. using hydrophobic membranes, or hydrophobic modification (i.e., large $\cos\theta$),
ii. using composite membranes with dense skin layers (i.e., small d_{max}),
iii. selecting liquids with high surface tension (i.e., large γ),
iv. increasing the compatibility between membranes and absorbents (i.e., avoiding membrane degradation),
v. optimizing operation conditions (i.e., maintaining transmembrane pressure < LEP).

Details of these anti-wetting methods will not be explored in this review as they can be found elsewhere [19,51].

In practical membrane contactor applications, controlling pressure gradients throughout the membrane module is a major operational problem, as unequal and uneven pressure drops in both the gas and solvent phases can lead to localized regions where the LEP is reached [37]. In a counter-current configuration, wetting often occurs near the solvent entry to the membrane module due to the pressure drop on the gas side. Therefore, in practical PCC applications the pressure drop on the gas side is generally limited to ~30 kPa, depending upon the feed gas pressure, the liquid phase pressure, and the membrane properties (e.g. pore size), to avoid membrane wetting and upstream compression. This requirement severely limits the type of modules that can be used. Standard hollow fiber bundles, which may be effective at bench scale, will not work on a larger scale. Significant pressure drops along the module length should be prevented because they can lead to significant changes in the transmembrane pressure, exacerbating membrane wetting.

3.2.2. Membrane fouling

Fouling (e.g., pore plugging) in membrane contactors receives much less attention than wetting. This is most likely because that membrane contactor technology for CO_2 removal from flue gas has not been commercialized, and most of the relevant research work is at bench or pilot scales, in which the flue gas is generally synthesized without contaminants (e.g., dusts or particles). A recent study introduced contaminants in flue gas and the results show that SO_2, water vapor and fine particles reduce CO_2 absorption performance in the membrane contactor [64]. In practical CO_2 removal from flue gas, fouling (including pore plugging) in membrane contactors may be a critical concern, because fine particles in flue gas can significantly increase mass transfer

Table 2
The glass transition temperature (T_g) and melting temperature (T_m) of polymers used as membrane materials in membrane contactors [234,235].

Polymer	Type	T_g (°C)	T_m (°C)
Polytetrafluoroethylene (PTFE)	Semi-crystalline	127	327
Polypropylene (PP)	Semi-crystalline	−20	176
Polyvinylidene fluoride (PVDF)	Semi-crystalline	~−30	~170
Polyethylene (PE)	Semi-crystalline	−115	137
Polyether ether ketone (PEEK)	Semi-crystalline	145	335

resistance [64,65]. Therefore, flue gas pre-treatment is needed to remove the contaminants and thus avoid fouling in membrane contactors. Further studies on membrane fouling in membrane contactors are important and would be well worth conducting.

3.2.3. Membrane degradation

Ideally, the membranes used in contactors should be thermally and chemically stable enough to maintain reasonable performance in long-term operations. In reality, however, the membranes are more likely to be attached by the chemical solvents [66,67]. The liquid absorbents after absorption of CO_2 are generally more corrosive [68,69], and they have stronger tendencies to change the membrane morphology, hydrophobicity and chemical structures, leading to membrane degradation and wetting, particularly at higher absorbent concentrations. The degradation products of solvents (e.g., amines) could also further damage the membrane.

In addition to chemical degradation, thermal degradation can be another problem. Not all membranes used in contactors have excellent thermal stabilities. Their dimensional stabilities depend upon the glass transition temperature (T_g) or the melting temperature (T_m) as discussed in Section 3.3.1 (Table 2). To avoid thermal degradation, robust polymers with relatively high T_g and T_m, such as PTFE and PEEK, should be selected for use in membrane contactors. Note that degradation of the glues used as the potting medium can be another problem when membrane degradation occurs.

3.3. Membranes in membrane contactors

In membrane contactor applications, membranes play an important role in absorption performance, even though they acting as non-dispersive barriers are not selective to CO_2. Typical membranes in membrane contactors are hollow fibers that are prepared with the selective skin layer on the outside. As a result, the solvent must be on the shell side to avoid membrane wetting, and the gas must flow on the lumen side. This configuration can also help minimize flow resistance of the solvent, particularly for the absorbent with a high viscosity.

Membranes in membrane contactors should have the following properties:

i. good thermal resistance to degradation at elevated temperature
ii. excellent chemical stability to the absorbent
iii. high hydrophobicity (i.e. low wetting tendency)
iv. high porosity to minimize the mass transfer resistance.

In the following sections, we will discuss research progress into the membranes used in membrane contactors, including hydrophobic microporous membranes, composite membranes with a dense skin layer, membranes incorporated with nanoparticles, or enzymes, and surface modified membranes.

3.3.1. Hydrophobic microporous membranes

Hydrophobic microporous membranes for use in membrane

Table 3
Factors affecting the structure-performance in membrane fabrication for CO_2 absorption.

Factors-membranes	Examples	Main remarks	Ref.
Additive-PVDF	Phosphorous acid, phosphoric acid, and glycerol	Pore-inducing agents; cause large pores (e.g. finger-like structures).	[49,83]
Additive-PVDF	Phosphoric acid, PEG, and glycerol	Pore-inducing agents; but cause sponge-like structures due to high viscosity of the dope solution.	[84]
Additive-PVDF	Ethanol	Pore-inducing agents; cause finger-like structures.	[84]
Additive-PVDF	LiCl	Pore-reducing agents; change the pore structure from finger-like to sponge-like and thus improve the long-term stability of the membrane.	[73]
Addictive-PES	O-xylene	Pore-reducing agents; reduce membrane pore size and permeability but increase the strength and contact angle.	[85]
Additive-PVDF	Hydrophobic macromolecules	Hydrophobicity-enhancing agents; improve the membrane hydrophobicity and wetting resistance as well as pore size, porosity and absorption performance.	[86,87]
Polymer concentration-PVDF	PVDF polymer	Membrane pore size and porosity reduce with an increase in polymer concentration.	[88]
Post-treatment-PTFE	Heating	Change membrane pore size distribution and porosity, and improve wetting resistance and absorption performance.	[76]
Inner coagulant-PVDF	Water, ethanol solution and DMAc solution	30 wt% DMAc solution can achieve inner skinless surface and higher CO_2 absorption flux; the inner skin layer is unavoidable when using ethanol solution or water as the internal coagulant.	[72]
Inner coagulant-PVDF	NMP solution	Increasing NMP concentration shifts the membrane morphology from a double-skin to a single-skin structure.	[74]
Fluid flow rates-PVDF	Dope and inner coagulant	High dope flow rates suppress the formation of macrovoids in inner region; high bore fluid flow rates suppress macrovoids in the sublayer.	[74]
Operating temperature-PVDF	Quenching and extrusion temperatures	High operating temperature causes large pore size and porosity.	[90,91]
Air-gap length-PVDF	Air-gas length	Achieve smaller pore size but best surface porosity, wetting resistance and absorption flux at the air-gas length of 10 cm.	[92]

contactors for CO_2 capture have been fabricated from many different polymers, such as PP [46–48,54,70,71], polyvinylidene fluoride (PVDF) [16,47–50,54,72–75], PTFE [23,47,70,76–78] polyethylene (PE) [79,80], and PEEK [38,81]. Khaisri et al. [47] compared the performance of the three most common materials (PP, PVDF and PTFE) used in membrane contactors and found that in physical absorption with water the PVDF membrane had a higher absorption rate than PP membranes, while in chemical absorption with MEA solutions absorption performance ranked in the order PTFE > PVDF > PP. These performance differences can be explained by the fact that membrane materials and structures determine the wetting tendency and thus affect absorption performance. PTFE membranes showed better long-term stability in 60-h of operation than PVDF, and better absorption performance [70] and wetting resistance [77] than PP over long-term operation. Mosadegh-Sedghi et al. [79] report that low density PE membranes are not compatible with amine solutions such as MEA due to absorbent intrusion and auto-oxidation. Addition of piperazine could effectively mitigate PE degradation due to its stabilizing effect.

Although these membrane materials have been intensively investigated in membrane absorption, they are not all thermally stable in desorption where the temperature can be 100–150 °C. Dimensional stability is generally indicated by T_g for amorphous polymers, or T_m for crystallized polymers (i.e., semi-crystalline with some degree of crystallinity). The T_g and T_m of the polymers commonly used in membrane contactors are shown in Table 2, which shows that all typical polymers used in membrane contactors are crystallized polymers. In practical operations, PP, PE, PVDF and potting glues may not be able to withstand the high temperature of desorption due to their relatively low melting temperatures. PTFE and PEEK are two excellent polymers for durable membrane contactor applications due to their relatively high T_m. Compared with PTFE, PEEK is less commonly used in membrane contactors for CO_2 capture. Recently, The GTI employed robust PEEK hollow fiber membrane contactors from PoroGen for CO_2 absorption and desorption [38,81].

A great deal of research has focused on hydrophobic microporous membrane fabrication. During membrane fabrication,

many factors significantly affect membrane structure, thereby influencing the ultimate membrane performance. Such factors include additives [49,73,82–87], polymer concentration [88], post-treatment [76], coagulant types, concentrations and flow rates [72,74,89], dope flow rates [74], operating temperature [90,91] and air-gap length [92,93]. These factors (including common examples) are summarized in Table 3, from which the following conclusions can be drawn:

i. Additives in the dope solution have four main roles:
   a. inducing membrane pore size and porosity,
   b. reducing membrane pore size and porosity,
   c. increasing membrane hydrophobicity,
   d. altering membrane pore size and porosity by changing the viscosity of the dope solution.
ii. Increasing polymer concentration (essentially the viscosity of the dope solution) decreases the membrane pore size and porosity, and vice versa.
iii. Post-treatments such as asymmetric heating can improve wetting resistance and absorption performance by altering the pore size distribution and membrane porosity.
iv. Inner coagulant type and concentration determine whether an inner skin occurs; an inner skin free structure offers lower mass transfer resistance and thus better absorption performance.
v. High dope flow rates or bore fluid (i.e., inner coagulant) flow rates can suppress macrovoid formation in the membrane and thus affect CO_2 absorption performance.
vi. High operating (e.g., quenching and extrusion) temperature leads to large membrane pore size and porosity.

3.3.2. Composite membranes with a dense skin layer

Since the hydrophobic microporous membrane in a membrane contactor is prone to being wetted by the liquid absorbent, selecting composite membranes with dense skin layers may improve both wetting resistance and chemical and/or thermal resistance of the membrane. This idea is proposed and validated by Kreulen et al. [55]. In their study, a membrane module coated with a thin (0.7 μm) permeable silicone rubber layer had comparable absorption rates to those with uncoated membranes. The dense skin
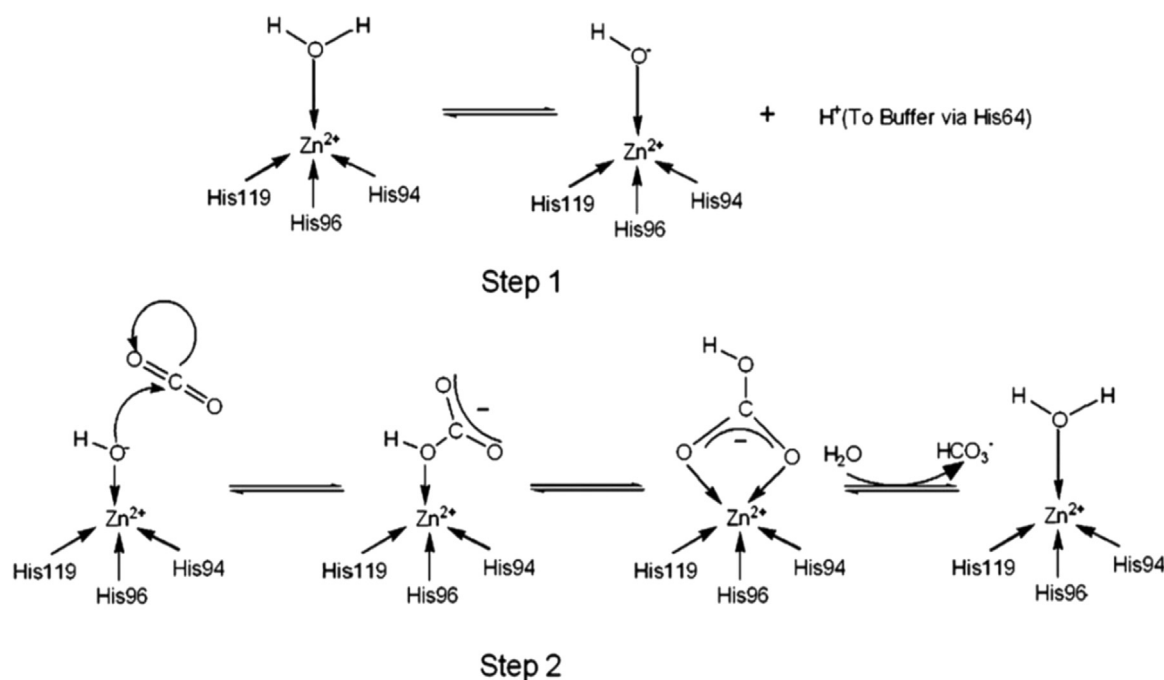
Fig. 4. CO$_2$ hydration mechanism of carbonic anhydrase [115].

layer should meet the following requirements:

i. be very thin (i.e., have negligible mass transfer resistance)
ii. have high CO$_2$ permeability
iii. have good chemical and thermal stabilities.

The most studied membrane materials for the dense skin layer are PDMS ($T_g = -125\ °C$) and poly(1-trimethylsilyl)-1-propyne (PTMSP, $T_g > 250\ °C$), which have CO$_2$ permeability of 4550 and 280,000 Barrer at ambient temperature, respectively [94–96].

Kneifel et al. [97] reported that a thin dense PDMS layer coated onto a polyetherimide surface can reduce the membrane permeability (by $\sim$20%). However, the reduction in membrane permeability after coating can be compensated for by the elevating the feed gas pressure (i.e., increase in driving force) due to the existence of the dense barrier. Li and Teo [98] observed that with an ultrathin skin layer, the feed gas side pressure can be maintained 200 kPa higher than the liquid pressure without any noticeable bubble formation in the liquid phase. Several elastomers, such as PDMS, ethylene propylene terpolymer, butadiene rubber, and styrene butadiene rubber have been tested as the dense skin layer materials in membrane contactors [99–102]. In reality, many commercial hollow fibers in membrane contactors are asymmetric composite membranes that have dense skin layers to prevent wetting and increase the range of their applications [18,55,103].

In addition, non-porous membrane contactors made of silicone rubber [104] or PDMS [37,102,105] have also been tested for CO$_2$ absorption. Even though the wetting issue of membrane contactors in long-term operations can be effectively solved, dense membranes incur significant mass transfer resistance and thus decreased absorption flux. Scholes et al. [37] observed that the non-porous PDMS membrane has an overall mass transfer coefficient two or three orders of magnitude less than PP or PTFE membranes, respectively.

More recently, Nguyen et al. fabricated a dense membrane contactor by coating two highly CO$_2$ permeable glassy polymers (PTMSP and Teflon-AF 2400) on porous PP supports [106]. The resultant membrane contactor has improved wetting resistance without sacrificing the overall mass transfer coefficient. The thin,

permeable, dense skin coating offers new opportunities for cheap supports (e.g., PP) to be used stably in membrane contactors over long time scales [77].

3.3.3. Nanoparticle incorporation

To improve membrane hydrophobicity and minimize mass transfer resistance, Zhang and Wang developed a highly porous polyetherimide hollow fiber membrane that incorporates fluorinated SiO$_2$ nanoparticles, and then performed surface hydrophobilization [107,108]. The resultant membrane exhibits improved hydrophobicity, absorption flux, mechanical strength and long-term stability. Rezaei et al. [109,110] fabricated new mixed matrix membranes (MMMs) by incorporating clay particles (e.g., general montmorillonite and Cloisite 15A) into PVDF. The resulting membrane contactors have better wetting resistance and CO$_2$ absorption rates.

3.3.4. Enzyme promotion

Recently, carbonic anhydrase (CA) has attracted growing interest in CO$_2$ capture processes [111–116]. CA is a metalloenzyme containing zinc metal ion as the active site, and known to catalyse the reversible hydration of CO$_2$ into bicarbonate (HCO$_3^-$) in aqueous solutions at extremely high turnover rates (up to $1 \times 10^6\ s^{-1}$) [117]. Therefore, CA has great potential to significantly enhance CO$_2$ absorption rates in PCC. The catalytic mechanism of CA works via a two-step process (Fig. 4) [115]. In the first step, the Zn^{2+} ion of CA combines with the hydroxide ion from a water molecule, releasing a proton; in the second step, the negatively charged hydroxide ion can attack the partially positive carbon atom on a solubilised CO$_2$ molecule, forming a bicarbonate (HCO$_3^-$) ion. The reaction mechanism of CO$_2$ hydration can also be expressed by the following equations [112,118,119]:

$$Zn^{2+} + H_2O \leftrightarrow Zn^{2+}OH^- + H^+ \tag{14}$$

$$CO_2 + Zn^{2+}OH^- \leftrightarrow + HCO_3^- + Zn^{2+} \tag{15}$$
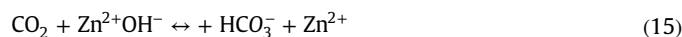
One of the most pronounced advantages of using CA in carbon capture is the ability to use environmentally benign solvents, such as water and potassium carbonate, which generally have slow

Fig. 5. Schematic of connection between membrane fouling mechanisms and enzyme immobilization strategies [123].

absorptive kinetics to CO_2. In membrane contactors, these solvents typically have lower wetting propensities than chemical solvents with higher CO_2 absorption rates. Thus, immobilizing CA in a membrane contactor may help overcome critical wetting problems.
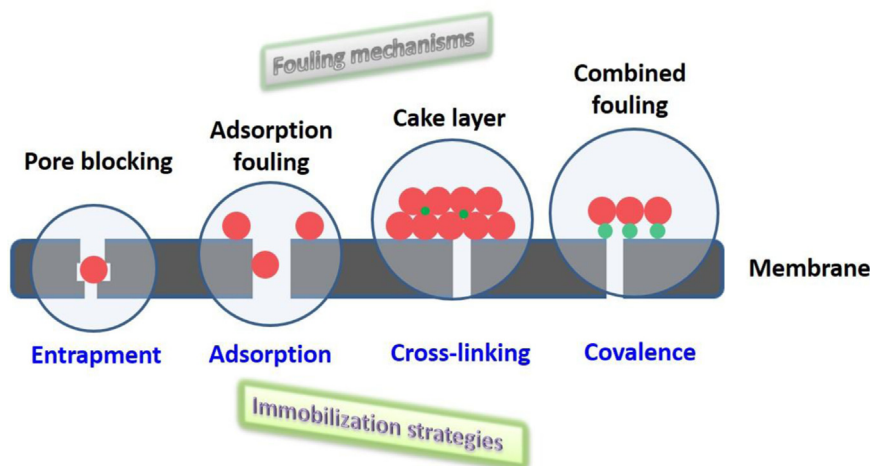
There are few studies on enzymatic membrane contactors. Early attempts of using CA in membrane contactors started with liquid membranes: CA was dissolved in a liquid layer between two hydrophobic gas permeable membranes [120,121]. However, trace contaminants in flue gas, such as SO_x and NO_x, will gradually dissolve in the liquid membrane and denature the enzyme. In addition, evaporation of the liquid will deteriorate the long-term operational stability of the liquid enzymatic membrane contactor. Enzyme immobilization has been proved as an effective approach to improve the reusability and stability of the biocatalyst.

Enzymes can be immobilized into or onto the membrane by entrapment (e.g. direct filtration) [122–124], physical adsorption [116,125,126], cross-linking [127] or covalent bonding [128–130]. These immobilization strategies are similar to membrane fouling mechanisms (Fig. 5) [123]. The entrapment method causes little enzyme activity loss [131], but significantly increases membrane resistance [124]. Physical adsorption based on the relatively weak physical forces (e.g., van der Waals and electrostatic) is a simple way to immobilize enzymes, but faces some issues, such as desorption and low enzyme activity [116]. Cross-linking and covalent bonding with multifunctional reagents offer stable enzyme immobilization; however, initial enzyme activity loss can be significant due to the activation of interface between the enzyme and the functional groups [132].

Various supports have been employed for CA immobilization,

such as hydrogels [115,130,133], polymeric membranes [127,129] and nanoparticle-incorporated membranes [116,134,135]. Hydrogels were selected as the immobilization support in which CA was filled into the interstitial space between two bundles of intimately commingled hydrophobic microporous PVDF hollow fiber membranes [115]. However, the major issues with the evenly distributed CA in the liquid phase are the low CO_2 diffusional gradient and large mass transfer resistance, which limit the full use of CA for hydration. Polymer membranes are also not ideal for enzyme immobilization due to the limited surface area and unfavorable interaction between the hydrophobic surface and the hydrophobic cores of the enzyme molecule, which would lead to enzyme distortion. Nanoparticles have high interfacial surface area, favorable hydrophilicity and controllable nanostructures, therefore offering great opportunity for enzyme immobilization. TiO_2 nanoparticles have been incorporated onto the membrane surface or into the membrane matrix for enzyme immobilization, achieving relatively high enzyme activity and stability [116,134,135].

In membrane contactor applications, it is difficult to preserve an intimate contact between CO_2, water and the enzyme immobilized on the hydrophobic membrane surface due to the naturally repulsive interaction between the hydrophobic surface and water. To overcome this issue, a "Janus" membrane configuration was proposed [136], where a hydrophobic layer acts as the fixed interfacial layer between gas and liquid, and a hydrophilic layer provides enzyme immobilization support that ensures intimate contact between CO_2, water and the immobilized CA (Fig. 6). With such a configuration the CO_2 hydration rate is almost doubled that of pure hydrophobic membranes within a gas–liquid membrane contactor.

The use of enzymes in CO_2 absorption systems is a biomimetic approach for improving CO_2 capture efficiency. The systems use enzymes (e.g. CA) to mimic the mechanism of the mammalian respiratory system, which dramatically increases CO_2 capture efficiency. CA can speed up the conversion of CO_2 to bicarbonate hydration and the reverse bicarbonate dehydration, and can catalyze the hydration of 600,000 molecules of CO_2 per molecule of CA per second: 4000 times faster than MEA in terms of catalytic activity [137].

In addition, CA can absorb CO_2 at neutral pH with very low heat of sorption. Since CA acts as a catalyst and has negligible capacity, it has been considered as the promoter for carbonate/tertiary amine systems [138–140]. However, CA is a natural enzyme with a limited life time ($\sim$6 months), and is sensitive to temperature and impurities. Loss of enzyme activity and long-term stability is the major drawback of CA membranes. As CA is either extracted from
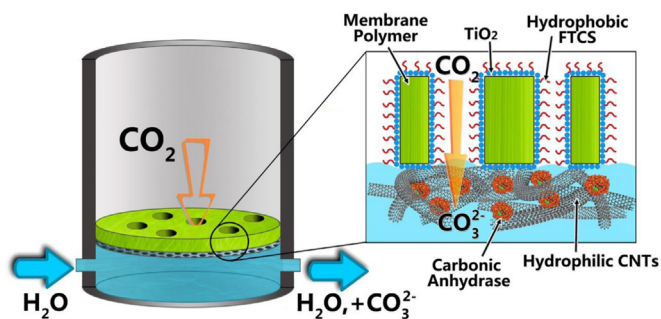

Fig. 6. Schematic diagram of the carbon nanotube functionalized Janus membrane for CO_2 hydration. Reproduced from [136] with permission from the Royal Society of Chemistry. FTCS: perfluorodecyltrichlorosilane; CNTs: carbon nanotubes.

mammals or cultured in labs, it is very costly and hence not feasible for use in large scale applications in conventional absorption columns. An alternative option is the use of CA in supported liquid membranes or membrane contactors [113,141]. A liquid membrane system (contactor) catalyzed by CA was developed by Carbozyme Inc. through a National Energy Technology Laboratory project (US). Preliminary results show the potential for significant decreases in energy penalty and costs compared with amine based systems [6]. An illustration of the process using CA in a contained liquid membrane is shown in Fig. 7 [6]. Both absorption and desorption occur simultaneously in the same contactor.

CA and mimic CA both increase the absorption rate of CO_2, rather than the equilibrium loading. A membrane contactor using 20% K_2CO_3 promoted by mimic enzyme (e.g., Zn-cyclen) was found to increase the CO_2 absorption rate by ~ 10 times [142].
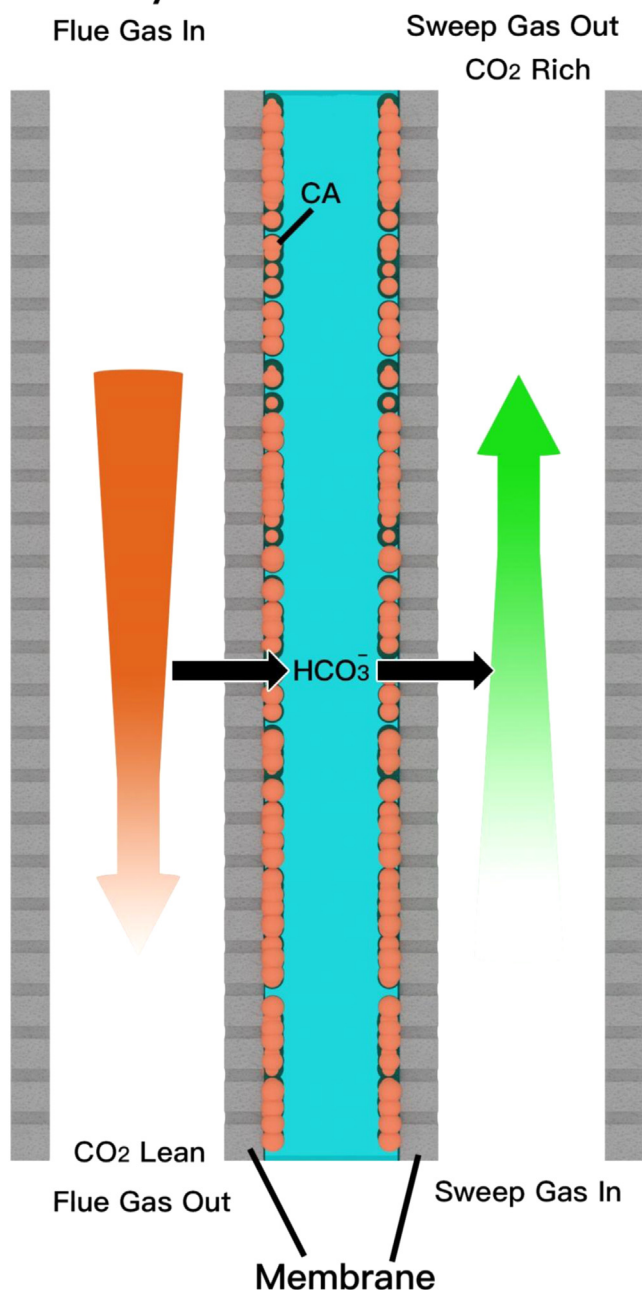

Fig. 7. Schematic illustration of the Carbozyme permeation process, modified from [6]. CA: carbonic anhydrase.

Enzymatic membrane contactors have the potential to employ environmentally benign solvents for efficient CO_2 absorption. However, they still face some challenges, such as increased mass transfer resistance after enzyme immobilization, and long-term enzyme stability and activity, which must be carefully considered before their use in CO_2 absorption.

3.3.5. Surface modification

A number of surface modification techniques have been investigated to improve membrane performance (e.g., wetting resistance, long-term stability and mass transfer coefficient). These techniques include plasma modification [71,143,144], non-solvent assisted deposition [145,146], sol–gel coating [147] and ultraviolet (UV) photografting [148].

PP membranes are frequently used as the substrate in surface modification, due to their low costs, good availability, well-controlled porosity and pore size and relatively high thermal and chemical stabilities. Lin et al. [71] employed CF_4 plasma to modify PP hollow fibers, showing that absorption flux, membrane durability and mass transfer coefficient of the treated membrane is significantly improved. Franco et al. [143,144] sputtered PTFE onto the PP membrane surface via plasma technique, forming an ultrathin fluorinated hydrophobic layer, and achieved improved absorption performance in short term (~ 45 h) due to the enhanced resistance to amine absorbent degradation and wetting after surface modification. However, the improved performance was not maintained for long. Lv et al. [145] deposited a rough PP layer onto the PP membrane surface using a mixture of cyclohexanone and methyl ethyl ketone (MEK) as the non-solvent. The modified surface showed superhydrophobicity (contact angle up to $158°$) and long-term stability (minimal CO_2 absorption flux decline over 20 days).

More recently, Lin et al. [147] fabricated hydrophobic polymethylsilsesquioxane (PMSQ) aerogel membranes onto an Al_2O_3 membrane support via sol–gel coating for CO_2 absorption in membrane contactors. The prepared membranes exhibited good durability and reusability. Yu et al. [149] developed a superhydrophobic ceramic membrane via surface modification as the membrane contactor for CO_2 absorption. The modified membrane had a water contact angle up to $153°$, and showed anti-wetting and anti-fouling properties. Since membrane contactors are expected to be operated over many months (preferably years) in practical CO_2 absorption, long-term performance stability after treatment is of great importance in adopting these surface modification techniques.

3.4. Absorbent selection

3.4.1. Absorbent selection criteria

Theoretically, any absorbents used in conventional absorption processes can be used in membrane contactors. However, some absorbent are more suitable when one considers their physical and/or chemical properties.

An ideal CO_2 absorbent should firstly have an appreciable absorption capacity (i.e., CO_2 loading), fast reaction rate, and preferably low heat of reaction. It should also be chemically stable, have negligible thermal and oxidative degradation, and be easily regenerated for recycling [8,150]. The solubility of CO_2 is a key parameter in the screening of potential solvents. A solvent with high CO_2 absorption capacity can effectively reduce the solvent volume and surface area required and hence the operational cost. High reactivity is another key factor, which leads to a high absorption rate and hence high mass fluxes, thus reducing the liquid phase resistance, which is usually the main contribution factor to the total resistance in a membrane contactor. From the environmental point of view, the absorbents and their degradation

compounds should be non-toxic to avoid harmful emission. Low vapor pressure or volatility, and good thermal stability will minimize solvent loss during operation and thermal degradation. Last but not least, the absorbent should preferably be commercially available at a low cost.

When selecting absorbents for membrane contactors, the interactions between absorbents and the membrane materials as well as configurations are primary considerations. An important prerequisite is good compatibility with the membrane materials used; the liquid absorbents should not damage the membrane either physically or chemically. If absorbents swell the membrane materials or attack the chemical structure of membrane materials, the surface/pore morphology of the membranes will be changed. In addition, an absorbent should preferably have high surface tension to provide a high critical LEP if a porous membrane is used. This will improve the pore-wetting resistance of the membrane. To reduce the overall mass transfer resistance, absorbents with low viscosity are favorable. High viscosity not only reduces the mass transfer rate, but also increases the pressure drop of the absorbent through the membrane contactor. Particularly, when a hollow fiber module is used or at reduced temperatures, high viscosity results in high energy consumption for absorbent circulation. The absorbents and their degradation compounds should not precipitate during the absorption because the solids formed may block the pores of the membranes, or even completely block the liquid path, resulting in a complete loss of efficiency.

As yet, no absorbent meets all these requirements. Some properties must be prioritized while others are sacrificed. In recent years, several less commonly "preferred" absorbents have been studied in membrane contactors to take advantage of their unique properties, such as ammonia (despite its high volatility), ionic liquids (ILs, despite their high viscosity) and enzymes (may be costly and difficult to produce).

3.4.2. CO_2 absorbents in membrane contactors

Both chemical and physical absorbents have been widely studied for CO_2 capture using membrane contactors. To date, chemical absorption of CO_2 (especially using amine aqueous absorbents) is the major PCC technology that has been practiced in the industry. Apart from amines, chemical absorbents such as ammonia, carbonates, alkali, amino acid salts and some types of ILs have also been investigated. However, these absorbents are still in the development or demonstration stage that needs to be commissioned before they can be implemented on a large scale.

Amines and their mixtures are the most investigated chemical absorbents for CO_2 capture. An amine is basically an organic compound derived from ammonia (NH_3), where one or more hydrogen atoms have been substituted with an alkyl or aromatic group. The ($-NH_2$) functional group of the amine molecule provides a weak base to react with acid gases. The reactivity of amines to CO_2 follows the order: primary > secondary > ternary amines [151]. MEA is the most widely used commercial CO_2 absorbent, usually in a 30 wt% aqueous solution. Most of the membrane contactors for PCC reported employ 30 wt% MEA as absorbents at temperatures between ambient and 313 K, offering a better comparison with the reference baseline conditions in a commercial absorption process [20,77,152].

Recently Chabanon et al. reported a membrane contactor operated with concentrated MEA solutions (up to 90 wt%) to intensify the process. They found that the intensification factor reached maximal with a MEA concentration of 70 wt% at 60 °C [153]. Investigation on a phase changing binary and ternary aqueous solutions of 2-(diethylamino)ethanol (DEEA) and 3-(methylamino)propylamine (MAPA) was reported to have significantly reduced energy consumption in desorption [154,155]. However, high volatility of these so-called 3rd generation solvents hinders their further applications. Most recently, the 3rd generation solvents have been employed in a membrane contactor with composite membranes consisting of a robust and highly gas permeable dense layer on the porous support for PCC [156].

The use of ammonia to remove acid gases was first reported in the 1950s. Since then, many publications have presented ammonia as a promising candidate for CO_2 capture from flue gas [8,157–159]. However, ammonia is a poisonous volatile gas with an intense odor and even small emissions may cause environmental issues. The feasibility of an ammonia based CO_2 capture process using hollow fiber membrane contactors was investigated [160]. Their CO_2 absorption experiments with ammonia were performed using two dense skin composite hollow fiber membranes, i.e. tailor made Teflon AF2400 and commercial TPX® (Polymethylpentene, PMP). Stable, good performance with reduced ammonia slip and intensified CO_2 mass transfer compared with a conventional packed column was reported. McLeod et al. report an aqueous ammonia absorbent for CO_2 capture with membrane contactors, in which ammonium bicarbonate crystals (as by-products) grow on the shell-side of the membrane by surface tension regulation [105].

Carbonate (alkali salt) is recognized as a green CO_2 absorbent. The reaction rate of potassium carbonate (K_2CO_3) with CO_2 could significantly be increased by raising the absorption temperature from 25 to 75 °C [161]. The main challenge in using this absorbent in a membrane contactor is the scaling of K_2CO_3 on and/or in membranes. Other challenges include the high loss of water when elevated temperature is applied, which results in humidification of the process stream and the requirement for a downstream dehumidifier. The industry has added amines (e.g., MEA, DEA and piperazine) to the absorbent to overcome these challenges, where the amine group acts as a promoter and the operating temperature can be lowered [162]. Most recently, enzymes have also been used to promote the CO_2 absorption rate of K_2CO_3 in membrane contactors [142].

A number of new solvents (e.g., amino acid salts and ILs) have been developed and studied in membrane contactors to enhance CO_2 absorption performance. Aqueous amino acid salts have been regarded as a new type of absorbents favorable for membrane contactors, as they provide both high active reaction with CO_2 and good compatibility with the membrane (i.e., friendly to membrane materials and low pore-wetting tendency) [163]. In addition, aqueous amino acid salts are nontoxic, thermally stable, easy to be regenerated, commercially available and have low vapor pressure. The reaction mechanism of amino acid salts with CO_2 is considered a zwitterionic mechanism, similar to primary and

Table 4
Properties and process conditions of typical physical solvents at ambient temperature [174].

Solvent	Viscosity (Pa s) $\times 10^3$	Surface tension	Tradename	Absorption conditions
Propylene carbonate	2.5	42	Fluor	T < ambient T, P: 3–7 MPa
Methanol	0.54	22.2	Rectisol	T: −10 to −70 °C, P > 1 MPa
N-methyl-2-pyrrolidone	1.7	34.4	Purisol	T: −20 to 40 °C, P: 1 MPa
Dimethylether polyethylene glycol	5.8	40.7	Selexol	T: 0–20 °C, P: 2–14 MPa
Ionic liquids	38–607	33–65	–	–

secondary amines [164,165].

The use of ILs as CO_2 absorbents has become a research highlight in recent years. ILs are commonly defined as organic salts with melting temperatures less than 100 °C, generally consisting of a large bulky and asymmetric organic cations and inorganic or organic anions. ILs can be classified into two categories: room-temperature ILs and task-specific ILs.

Luis et al. proposed a "zero solvent emission process" concept using ILs in membrane contactors for PCC [166,167]. They used a commercially available cross-flow membrane contactor supplied by Liqui-Cel and 1-ethyl-3-methylimidazolium ethylsulfate as the IL solvent, and reported that the bottleneck of the membrane absorption process is the slow interfacial chemical reaction between CO_2 and ILs. Deng et al. [168] reported a closed loop, continuous pressure swing absorption/desorption process for CO_2 capture at elevated temperatures by using ILs with relatively low viscosity, including room-temperature ILs and IL-based solvents consisting of task-specific ILs (e.g., amino acid ILs) and low molecular weight polymers polyethylene glycol (i.e., amino acid ILs/PEG). Sirkar et al. [169,170] developed a pressure swing, membrane absorption/desorption process with viscous chemical sorption ILs in a stationary phase as CO_2 absorbent (poly(amidoamine) dendrimer-[bmim][DCA] mixture), and a process mimicking the conventional pressure swing adsorption cycle. Good CO_2 separation performance is reported [169–171]. Recent advances in the combination of ionic liquids with membrane absorption technology for CO_2 capture have been reviewed [172].

Well-known physical absorbents include propylene carbonate (a.k.a. *Fluor Solvent*), methanol (a.k.a. *Rectisol*), dimethyl ethers of polyethylene glycol (DMPEG, a.k.a. *Selexol*) and N-methyl-2-pyrrolidone (a.k.a. *Purisol*), which are mostly used in different industrial sectors for CO_2 separation or purification at high pressures, and the absorption usually processes at a temperature lower than the ambient temperature. For instance, when using Selexol as CO_2 absorbents, the process generally takes place at 0–5 °C. A recent research reported that the optimal operating temperature in the lean Selexo solvent is -10 °C [173]. The properties and process conditions of major physical solvents are summarized in Table 4, where ionic liquids are included as one category of solvent for comparison [174].

3.5. Module design

The membrane module configuration plays an important role in determining the performance of membrane contactors. In a gas–liquid membrane contactor, the membrane module should provide an efficient gas–liquid interface without convective flow of fluid through the membrane (i.e., non-dispersive gas–liquid contact). Both flat sheet and tubular membrane modules can be used in a gas–liquid membrane contactor.

A flat sheet membrane module can be mounted in a plate-and-frame configuration for membrane contactor applications. As the membrane area in a flat sheet membrane module is much lower than that in a hollow fiber module, few studies reported the use of flat sheet membrane contactors for CO_2 separation applications [150,175–177]. Their main advantages over hollow fiber membrane contactors are ease of membrane fabrication and module assembly.

A tubular membrane module generally refers to the hollow fiber membrane module (inner diameter < 1.0 mm) [178]. Hollow fiber membrane contactors have been widely investigated for CO_2 capture with a broad range of absorbents. It should be noted that in a few cases tubular membranes with an inner diameter (> 5 mm) larger than that of a hollow fiber membrane are also used to minimize the pressure drop in PCC, for both polymeric and inorganic membranes.

A hollow fiber module is typically a bundle of fibers packed parallel in a shell, similar to the configuration of a shell and tube heat exchanger. As most hollow fiber membranes have the skin layer on the outside, the liquid phase in a hollow fiber membrane contactor is usually on the shell side to minimize membrane wetting; whereas gas flows on the lumen side, which is also beneficial for the reduction of pressure drop along the membrane. Although many different kinds of membrane module configurations have been developed, hollow fiber membrane modules with longitudinal flow or cross flow are the most extensively studied for CO_2 capture. Yang et al. [179] studied both longitudinal and cross flow hollow fibers for gas liquid contact and found that the cross flow membrane contactors show better absorption performance. Nevertheless, most research work has been carried out using longitudinal module design, due to its simplicity [179].

3.5.1. Longitudinal flow module

Longitudinal flow is also called parallel flow. In this configuration, both fluids (gas and liquid) flows parallel to each other on the opposite sides of a membrane, either in a co-current or counter-current flow (Fig. 8A) [19,21]. deMontigny et al. [70] showed that the mass transfer rate in counter-current mode is 20% higher than that in co-current mode, and that absorbents flowing on the lumen (tube) side of the fiber perform better than the other orientation when the inner diameter of the fiber was not prohibitive to flow. Most lab-scale studies have been conducted with longitudinal design membrane contactors due to the ease of preparation, well-defined fluid dynamics and simple approach towards mass transfer calculations. However, compared with a cross flow module, a longitudinal module offers limited efficiency [20]. Channeling and bypassing of fluid on the shell side and high shell-side pressure drop may affect the overall performance of the system, while fluid flow is restricted by the non-uniform packing and small internal diameter of hollow fibers, which also limits mass transfer and gives relatively low mass transfer coefficients [180]. These are the major barriers to the use of this type of
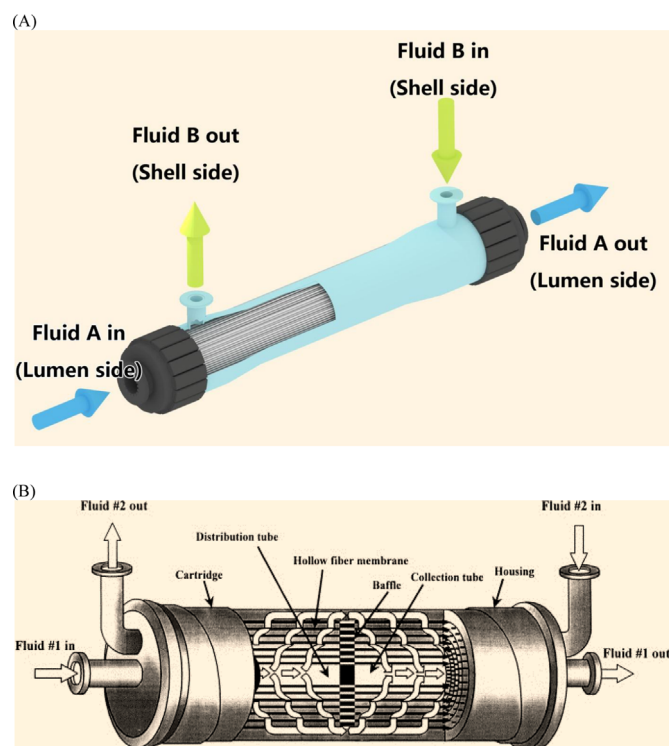
Fig. 8. (A) Parallel flow module (counter current flow); (B) Liqui-Cel Extra-Flow membrane contactor [183].
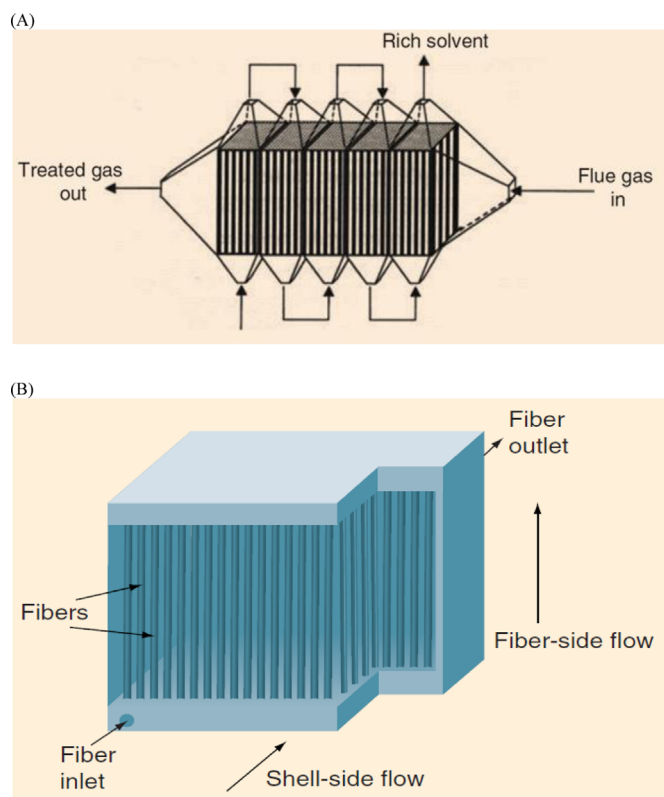
(A)

(B)

Fig. 9. Cross-flow membrane contactor modules developed by (A) Aker Kvaerner [187]; (B) the Netherlands Organization for Applied Scientific Research (TNO) [21].

module in industrial applications [12,181,182].

Modifications to longitudinal modules have been made to combine the advantages of cross-flow and improve mass transfer in the module. A well-known commercial example is the Liqui-Cell Extra-Flow module offered by CELGARD LLC (Charlotte, NC; formerly Hoechst Celanese) [183]. An illustration of this gas–liquid hollow fiber membrane contactor module is given in Fig. 8B.

A central baffle in the shell side of the membrane contactor minimizes shell-side bypassing and provides a velocity towards the membrane surface, which results in a higher mass transfer coefficient than that achieved with a strictly parallel flow (Fig. 8A).

This module allows both counter-current contacting and flow perpendicular to the well-spaced hollow fibers. The counter-current contacting increases the number of transfer units involved in a given separation, and the perpendicular flow gives mass transfer coefficients typically five times larger than those available with other modules [184].

3.5.2. Cross-flow module

Although longitudinal flow modules have been the most studied, the cross-flow module is considered more efficient. Experiments with a rectangular cross flow membrane contactor were carried out for physical absorption of gas to study the effects of various operating parameters (e.g., gas and liquid flow rates and solute concentration in the feed stream) on overall performance of the system [185]. The performance of the longitudinal and cross-flow membrane contactors was compared based on the flow per membrane area and the equal module volume [186]. It was found that counter-current cross-flow membrane contactors are more efficient. Two examples of cross-flow membrane contactors individually patented by Aker Kvaerner (Norway) and TNO (the Netherlands) are respectively presented in Fig. 9A [187] and Fig. 9B [21,25,185].

3.6. Mass transfer and process simulation

In this section, we aim to define the modeling conditions and/ or different notations used by researchers to avoid confusion, and discuss four types of modeling approaches in detail, which are widely used for CO_2 absorption with membrane contactors. The modeling and simulation of membrane contactors for PCC applications has been extensively investigated for decades [10,19,21,152,188,189]. The modeling framework is basically similar to that used for absorption column simulation, but the membrane mass transfer description requires dedicated approaches. A general sketch of mass transfer of different compounds in membrane contactors (Fig. 10). It should be stressed that, for the sake of simplicity, CO_2 absorption is almost systematically considered as the only mass transfer phenomenon in modeling approaches.

A considerable amount of knowledge and experience can be gained from the literature dedicated to CO_2 absorption into chemical solvents by packed columns, including at industrial scale
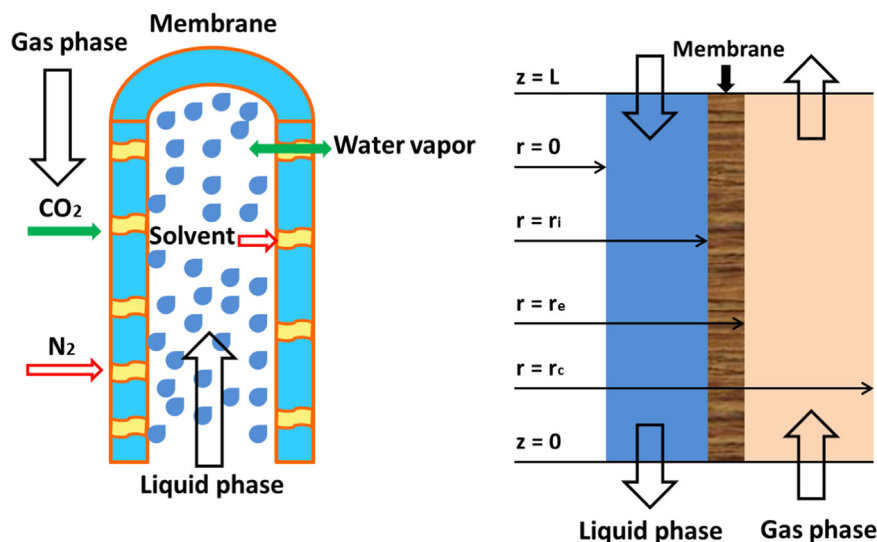
Fig. 10. Framework of mass transfer modeling in membrane contactors for post-combustion carbon capture. Absorption of CO_2 from the gas phase to the liquid phase is the major target of the process. Mass transfer of N_2, solvent and water vapor is considered to be insignificant. Water vapor transfer is complex because it is likely to occur either from the gas to the liquid (condensation) or from the liquid to the gas phase (evaporation) depending on the operating condition and location.

INPUT VARIABLES

Operating conditions

Temperature
Pressure
Feed composition
Gas and liquid velocity

Membrane & module

Membrane and
module characteristics
(mass transfer,
geometry)

Solvent

Chemical solvent
characteristics
(concentration, kinetics,
viscosity...)

Modelling
&
Simulation

Prediction of
performances for
operating conditions

Optimal operating
conditions

Scale up

Guidelines for
membrane, fiber
and module
performances

Optimal
module design

Integration in
PSE for overall
CCS process
simulation

Fig. 11. General sketch of process modeling and simulation for membrane contactor applications in a post-combustion carbon capture framework. CCS: carbon capture and storage.

[190–195]. Many publications have addressed the modeling/simulation problem for the specific case of membrane contactors for CO_2 absorption in a chemical solvent and a large portfolio of models has been reported. The ultimate target of these studies is to predict experimental results through a large range of operating conditions and systems with a minimal number of adjustable parameters. A key problem with modeling is finding a balance between model complexity, numerical resolution and the possibility of precisely estimating the maximal number of variables in the simulation set, to completely predict process performances.

Fig. 11 summarizes the key variables that must be defined when simulating the absorption performance of a membrane contactor for PCC and the different targets of modeling/simulation studies. 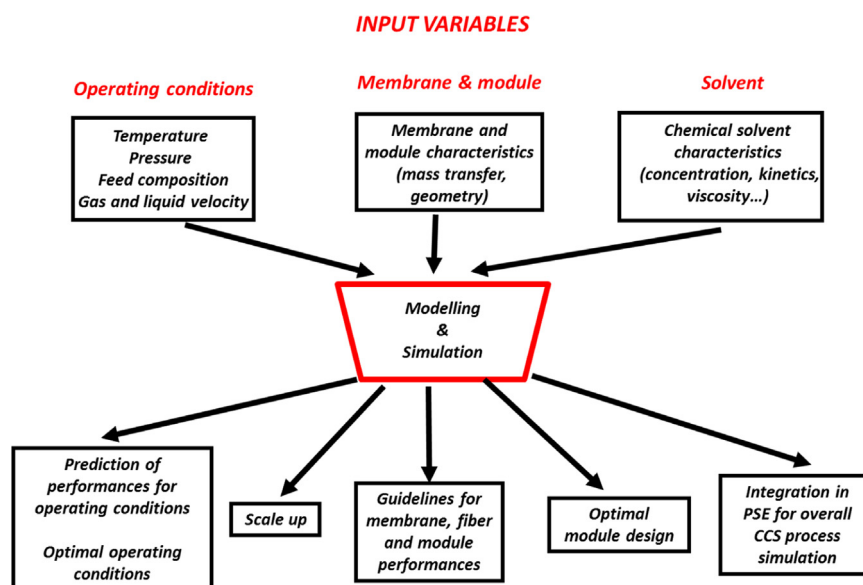Generally speaking, a large number of studies are limited to a comparison of a set of experimental data to the predictions of one type of model. Several publications make use of a given model for parametric sensitivity studies (e.g. prediction of the influence of gas or liquid velocity, or membrane mass transfer coefficient on absorption performances). Very few comparative studies evaluating different models have been published. Similarly, optimization and scale-up problems are largely unreported.

3.6.1. Modeling approaches: overall framework

The starting point of any modeling problem corresponds to the definition of a set of hypotheses concerning the physical and chemical characteristics of the system. The steady state condition hypothesis is almost systematically applied, similarly to the absorption column reference case. As proposed in Fig. 11, the input variables in a modeling and simulation study can be classified into three main categories: (i) operating conditions, (ii) membrane and module characteristics, and (iii) solvent characteristics.

The absorption of CO_2 from a dry CO_2/N_2 gaseous stream into an aqueous solution of MEA through a lab-scale membrane contactor unit is by far the most often investigated system and will be taken as the reference case (a dry CO_2/N_2 mixture is often employed as the flue gas in modeling). In many cases, flue gas with a CO_2 content of 10–15 vol% is selected to mimic the real situation in a coal-fired power plant. Temperature is usually close to ambient conditions (20–40 °C) and gas pressure is atmospheric, which is similar to packed column operation for CO_2 absorption. The module geometry is most often of hollow fiber type, with

dimensions of a few centimetres in diameter and 10–30 centimetres in length in most cases. Flat or spiral module geometry is rarely applied. A broad range of fiber geometries, membrane materials and structural characteristics can be found, with membrane thicknesses ranging from 20 to 500 μm. The module packing ratio typically varies between 0.1 and 0.6. In terms of fluid flow conditions, two major options are possible:

- Liquid inside: liquid solvent on the lumen side and gas flowing on the shell side. This configuration is advantageous for industrial applications, because it can better fit the very large gas flow rate (possibility to provide a larger cross-section area for gas flow). Note: in this configuration, wetting is more likely to occur due to the high lumen-side pressure caused by the constrained liquid flow; limited liquid flow may be another issue particularly when the liquid is viscous.
- Liquid outside: liquid solvent on the shell side and gas flowing on the lumen side. This option is also widely studied because standard hollow fibers need liquid solvent on the shell side to minimize the flow resistance of the liquid. It offers a larger gas–liquid interfacial area, at the expense of an increased pressure drop on the gas phase and risk of fiber blocking by dust particles in practical flue gas application.

When the operating conditions and membrane and module characteristics are defined, mass (and, in some cases, energy) balances and transfer equations can be developed, according to a specific set of hypotheses.

3.6.2. Modeling approaches: state of the art

An exhaustive analysis and description of the different modeling options offered through the combination of possibilities is far beyond the scope of this review. A critical description of four families of models with gradual complexity, which are the most often encountered in the literature, is proposed as follows.

Note that regardless of the level of complexity of the mathematical approach selected, the models are developed based on a single hollow fiber representative approach (Fig. 10) [196].

3.6.2.1. Model based on constant overall mass transfer coefficient (K). The constant overall mass transfer coefficient approach is the

first and simplest model reported in the literature dedicated to membrane contactors [14,15,186,197]. In this approach, K is supposed to stay constant between the inlet and outlet of the membrane module. For a membrane contactor with an effective length of L, the differential CO_2 mass balance can be easily integrated. The effective CO_2 capture ratio (η), the key performance indicator of the process, can be expressed as follows:

$$\eta = 1 - \exp\left(\frac{-K\,a\,L}{u_g}\right) \tag{16}$$

where a is the interfacial area and u_g is the gas velocity. Ka corresponds to the inverse of the CO_2 transfer time in the process, which is a key parameter allowing comparison of gas absorption technologies and evaluation of scale-up possibilities. The term $\frac{K\,a\,L}{u_g}$ determines the process mass transfer performance.

This model is easy to use once the evolution of the capture ratio (η) with the gas velocity (u_g) is experimentally determined. Its major limitation comes from the fact that K is often by no means a constant but depends on the operating conditions. In most cases, K varies along the axial position and the direction of the driving force. In such situations, Eq. (16) no longer applies and more rigorous models (e.g. the following ones) are required.

3.6.2.2. Resistance-in-series (1D) model. The resistance-in-series model was detailed in Section 3.1. This modeling approach is based on the film theory. The local overall mass transfer coefficient (K) is expressed for a flat geometry as follows:

$$\frac{1}{K} = \frac{1}{k_g} + \frac{1}{k_m} + \frac{1}{m\,E\,k_l} \tag{17}$$

where m is the CO_2 gas–liquid partition coefficient (-).

Theoretically, each local mass transfer coefficient (k_g, k_m and k_l) can be estimated based on correlations. For k_g and k_l, expressions based on the Sherwood number have been reported in the literature [10,48]:

$$k_g = Sh_g \frac{D_g}{d} \tag{18}$$

$$k_l = Sh_l \frac{D_l}{d} \tag{19}$$

where D_g and D_l are the CO_2 diffusion coefficients in the gas and liquid phases, respectively ($m^2\,s^{-1}$), and d is the diameter (m).

Generally, the membrane mass transfer coefficient is supposed to be constant and used as the only adjustable parameter to fit the data. It can be theoretically calculated by:

Fig. 12. Cross-section of the membrane module and circular approximation of the fluid surrounding the fibers according to the Happel's free surface model, modified from [201].

$$k_m = \frac{D_m \epsilon}{\tau \delta} \tag{20}$$

where D_m is the CO_2 diffusion coefficient in the membrane ($m^2\,s^{-1}$), ϵ is the membrane porosity (-), τ is the membrane tortuosity (-) and δ the membrane thickness (m).

The local enhancement factor (E) due to the reaction between the MEA and CO_2 in the liquid phase can be determined by the Hatta number (Ha) and the infinite enhancement factor (E_∞) [59,198]:

$$Ha = \frac{\sqrt{D_l kr\, C_{MEA,l}}}{k_l} \tag{21}$$

$$E_\infty = \left(\frac{D_l}{D_{MEA}}\right)^{1/3} + \frac{C_{MEA,l}}{2C_{CO_2,l-int}}\left(\frac{D_l}{D_{MEA}}\right)^{-2/3} \tag{22}$$

where kr is the kinetic constant ($m^3\,mol^{-1}\,s^{-1}$), $C_{MEA,l}$ is the MEA concentration in the liquid phase ($mol\,m^{-3}$), D_{MEA} is the MEA diffusion coefficient in the liquid phase ($m^2\,s^{-1}$) and $C_{CO_2,l-int}$ is the CO_2 concentration in the liquid phase at the membrane interface ($mol\,m^{-3}$).

Hence, according to the reaction regime, the enhancement factor is expressed as follows:

- The diffusion of MEA is not limiting (the reaction is distributed but located in the vicinity of the gas–liquid interface):

$$\frac{E_\infty}{Ha} > 50,\ \text{then}\ E = \sqrt{1 + Ha^2} \approx Ha$$

- The diffusion of MEA is limiting (a sharp reaction front is formed in the vicinity of the gas–liquid interface):

$$\frac{E_\infty}{Ha} < 0.02,\ \text{then}\ E = E_\infty$$

- Partial limitation of MEA diffusion (intermediate situation):

$$0.02 \leq \frac{E_\infty}{Ha} \leq 50,\ \text{then}\ E = \frac{Ha\sqrt{(E_\infty - E)/(E_\infty - 1)}}{\tanh\left(Ha\sqrt{(E_\infty - E)/(E_\infty - 1)}\right)}$$

The resistance-in-series model requires the boundary conditions at the inlet and outlet of the module to be defined (i.e., c and P at $z = 0$ and $z = L$) to solve these equations.

3.6.2.3. Convection diffusion (2D) model. Instead of the 1D effective mass transfer coefficient description, more refined models have been proposed based on a general convection diffusion approach [54,59,196,199,200]. Convection and diffusion are then separately taken into account in the gas and liquid phases.

Generally, the convection diffusion model considers the solvent concentration gradient in the liquid phase and the CO_2 concentration gradient in both liquid and gas phases, the chemical reaction between CO_2 and MEA in the liquid phase and the decrease of the gas velocity due to CO_2 absorption.

The set of differential mass balance equation system for CO_2 in the gas and liquid phases, and MEA in the liquid phase in cylindrical coordinates are respectively expressed as:

$$u_{z,g}\frac{\partial C_{CO_2,g}}{\partial z} = D_g\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{CO_2,g}}{\partial r}\right)\right] \tag{23}$$

$$u_{z,l}\frac{\partial C_{CO_2,l}}{\partial z} = D_l\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{CO_2,l}}{\partial r}\right)\right] + R_{CO_2} \tag{24}$$

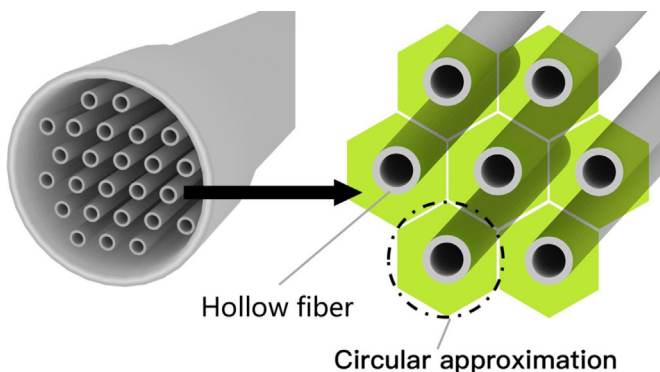$$u_{z,l}\frac{\partial C_{MEA,l}}{\partial z} = D_{MEA}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{MEA,l}}{\partial r}\right)\right]+2R_{CO_2} \tag{25}$$

where the stoichiometric constraint due to the chemical reaction between CO_2 and MEA can be described by:

$$u_{z,l}\frac{\partial C_{MEA,l}}{\partial z} = -2u_g\frac{\partial C_{CO_2,g}}{\partial z} \tag{26}$$

CO_2 transfer in the membrane is assumed to result from the contribution of diffusion. Consequently, mass balance in the membrane can be expressed through Fick's law:

$$D_{meff} = \left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{CO_2,m}}{\partial r}\right)\right]=0 \tag{27}$$

The flow on the lumen side of the membrane is assumed to be a fully-developed laminar parabolic flow, as confirmed by the low Reynolds number:

$$u^{lumen}=2\langle v\rangle\left[1-\left(\frac{r_i}{r}\right)^2\right] \tag{28}$$

The flow on the shell side of the membrane contactor is often modeled using the Happel's free surface model (Fig. 12) [201,202]:

$$u^{shell}=2\langle v\rangle\left[1-\left(\frac{r_e}{r}\right)^2\right]\left[\frac{(r/r_c)^2 - (r_e/r_c)^2+2\ln(r_e/r)}{3+(r_e/r_c)^4-4(r_e/r_c)^2+4\ln(r_e/r_c)}\right] \tag{29}$$

with

$$r_c = r_e\sqrt{\frac{1}{1-\varphi}} \tag{30}$$

In the convection diffusion approach, the boundary conditions are:

- Axial direction (assuming counter-current flow pattern)

  $z=0$, $c_i^{lumen}=0$ for $i=CO_2$, & $c_i^{lumen} = c_{i,in}^{lumen}$, for $i=MEA$

  $z = L$, $c_i^{shell} = c_{i,in}^{shell}$ for $i=CO_2$, & $c_i^{shell}=0$, for $i=MEA$

- Radial direction

  $r=0$, $\frac{\partial c_i^{lumen}}{\partial r}=0$ for $i=$all species,

  $r = r_i$, $\frac{\partial c_i^{lumen}}{\partial r}=0$ for $i=$amine species & $c_i^{lumen} = mc_i^{mem}$, for $i=CO_2$

  $r = r_o$, $c_i^{mem} = c_i^{shell}$ for $i=CO_2$ & $c_i^{mem}=0$, for $i=MEA$

  $r = r_g$, $\frac{\partial c_i^{shell}}{\partial r}=0$ for $i=CO_2$ & $c_i^{shell}=0$, for $i=MEA$

3.6.2.4. Model for non-isothermal systems. A few authors [203,204] report a similar convection diffusion approach but under non-isothermal conditions. In this case, a set of differential energy balances has to be added to the mass balances:

$$\kappa^{shell}\left[\frac{\partial^2 T^{shell}}{\partial r^2} + \frac{1}{r}\frac{\partial T^{shell}}{\partial r}\right] = \rho C_p v_z^{shell}\frac{\partial T^{shell}}{\partial z} \tag{31}$$

$$\kappa^{mem}\left[\frac{\partial^2 T^{mem}}{\partial r^2} + \frac{1}{r}\frac{\partial T^{mem}}{\partial r}\right]=0 \tag{32}$$

$$\kappa^{lumen}\left[\frac{\partial^2 T^{lumen}}{\partial r^2} + \frac{1}{r}\frac{\partial T^{lumen}}{\partial r}\right] + \rho\sum H_i^{lumen} = \rho C_p v_z^{lumen}\frac{\partial T^{lumen}}{\partial z} \tag{33}$$

In the non-isothermal approach, the mass balance equations are the same as those in the convection diffusion model, thus the same boundary conditions are used. However, with the added energy balance equations, the following set of boundary conditions is required:

- Axial direction

  $z=0$, $T^{lumen} = T_{in}^{lumen}$

  $z = L$, $T^{shell} = T_{in}^{shell}$

- Radial direction

  $r=0$, $\frac{\partial T^{lumen}}{\partial r}=0$

  $r = r_i$, $T^{lumen} = T^{mem}$

  $r = r_e$, $T^{mem} = T^{shell}$

  $r = r_c$, $\frac{\partial T^{shell}}{\partial r}=0$

The different sets of assumptions for the above four approaches are summarized in Table 5. A tentative analysis of the corresponding situation that best fits the set of hypotheses is also proposed.

3.6.3. Unexplored issues

Despite considerable efforts made into modeling and simulations of membrane contactors in PCC, several issues remain largely unexplored. We propose here a tentative list of important needs and challenges in this area.

3.6.3.1. Tackling non-isothermal conditions. The isothermal condition, which is extensively employed in membrane contactor studies, is one of the major differences between membrane models and standard models for packed columns. The incidence of non-isothermal behaviors in simulation results has only recently been investigated [78,199,203–207]. Experimental evidence and basic calculations show that a significant temperature difference occurs in a membrane contactor, principally due to the heat of reaction contribution (i.e. CO_2 reaction with amines in the liquid phase). Nevertheless, the good prediction efficiency of models based on an isothermal hypothesis suggests that compensation effects may take place. Further studies, ideally combining simulations and experiments (with temperature profile monitoring), are required to better understand the need to take temperature changes in the membrane contactor into account. Note that temperature increase is overestimated when CO_2 absorption and reaction is taken as the sole phenomenon.

A completely different picture is obtained when the role of water is considered in the simulation package. Water condensation and/or evaporation generate large energy fluxes, which can in some cases significantly counterbalance the heat of reaction incidence on temperature variation. In such cases, both non-isothermal hypothesis and water behaviors should be taken into account to achieve relevant and effective description. This point is discussed further below.

3.6.3.2. The role of water. In most simulations of membrane

Table 5
Summary of the four types of models proposed in membrane contactor modeling and the corresponding situations.

Modeling strategy	Assumptions	Remarks (pros/cons)	Ref.
Constant overall mass transfer coefficient (K)	1. T, P, K and Q_g are constants; 2. Low $C_{CO2,l}$ 3. Plug flow in the gas phase; 4. Adjusted parameter K	Fresh solvent at the inlet with a large excess ($\alpha_{in} \sim \alpha_{out} \sim 0$). Pros: simplest approach; minimal information needed; enables comparison with literature data. Cons: not rigorously applicable to industrial situations; lumped K variable combining solvent and membrane mass transfer performances.	[14,15,186,197]
Resistance-in-series (1D)	1. T, k_g and k_l are constants 2. C_{MEA}, ΔC and P are variables 3. Plug flow in the gas and liquid phases 4. Chemical reaction considered 5. Adjusted parameter: k_m	Classical approach for various inlet and outlet solvent conditions. Pros: good prediction of mass transfer when K_m is known. Cons: not rigorously applicable to industrial situations.	[198,236]
Convection diffusion (2D)	1. T and P are constants 2. Axial convection and radial diffusion in the liquid and gas phases 3. Chemical reaction considered 4. Adjusted parameter: k_m	Classical approach for various inlet and outlet solvent conditions; be equivalent to the resistance-in-series approach reported by some researchers. Pros: applicable to real absorption situations (no assumption of fresh amine excess); roles of the membrane, solvent and hydrodynamic can be evaluated separately; probably the best compromise in terms of complexity and prediction efficiency.	[54,59,196,199,200]
Non-isothermal system (2D)	1. P is a constant 2. Axial convection and radial diffusion in the liquid and gas phases 3. Chemical reaction considered 4. Adjusted parameter: k_m	Complicated and rarely reported; many variables required; water and non-isothermal behaviors should be considered simultaneously; could be used for better prediction and/or pilot scale studies; experimental temperature profile remains difficult to predict.	[203,204,237]

contactors for PCC, CO_2 is regarded as the only compound transferring from the gas to the liquid phase. This hypothesis considerably simplifies the set of equations to be solved and overlooks the influence of water in modeling of lab-scale data (dry gas is typically used). In reality, flue gas from power stations contains water vapor. Water transfer also occurs in membrane contactors, either from the gas to the liquid phase (i.e., condensation) or from the liquid to the gas phase (i.e., evaporation). The local water driving force (partial pressure difference between the liquid phase and gas phase) can effectively generate evaporation effects (e.g., at the gas inlet when a dry feed gas mixture is used in the experiments), or condensation effects (e.g. at the liquid outlet when temperature drops below the dew point of the gas mixture). Visual observations of water droplets at the outlet of membrane contactors have been occasionally reported and support this statement.

Unfortunately, water balance studies have not been experimentally performed and the modeling of water behaviors requires a complex set of equations to be added to the simulation package. More specifically:

- water pressure calculations require an effective thermodynamic model for the liquid phase (activity coefficient calculation),
- water transfer in the membrane can be complex due to capillary condensation effects,
- the calculation of local temperature conditions through energy balance computations requires coupled heat and mass transfer systems to be solved.

It is worth to note that water transport is even more important in membrane desorption, particularly for understanding the energy balance.

Overall, water plays an important role in modeling CO_2 capture via membrane contactors, but relevant investigations are scarce due to experimental limitations (gas phase humidity and temperature measurements, and water balance calculations) and model complexity (coupled processes with numerous variables). Alternative mass transfer models, such as the Maxwell-Stefan approach used for multicomponent systems, could be of interest for better prediction [208].

3.6.3.3. Prediction of membrane mass transfer coefficient considering local variations, long time scales and wetting effects. The membrane mass transfer coefficient (k_m) is most often taken as an adjustable parameter in membrane contactor modeling. An overall effective mass transfer coefficient is thus assumed, with a large uncertainty in terms of prediction mostly due to wetting effects [152]. Minor and even local partial wetting can significantly affect the overall k_m value [77]. Given the impossibility of determining the exact wetting intensity throughout the membrane radial and axial directions, a global approach has been logically employed [51,54,66]. The intrinsic complexity of the underlying situation that gives rise to the global k_m value is presented in Fig. 13A. The effect of wetting intensity on the membrane mass transfer coefficient is shown on Fig. 13B.

Accurate prediction of the partial wetting effects is extremely challenging because of the complexity of the membrane pores (e.g. pore size distribution and pore geometry). To our knowledge, no in-situ measurement of local wetting in a membrane contactor under operation has been reported to date. This target could possibly be achieved by non-invasive measurement techniques, like nuclear magnetic resonance, similar to studies of the wetting of polymeric membranes used in fuel cells. Given the sensitivity of membrane wetting to the local transmembrane pressure, the effective k_m value could depend on operating conditions (even for the same membrane); for example, variation in the gas or liquid velocity will change the pressure gradient [204]. This hypothesis can partly explain the large variation in effective mass transfer coefficients reported in different studies.

Apart from the variation and difficulty of prediction of the membrane mass transfer coefficient under steady-state operation, the rapid or gradual change of k_m over time is another major challenge. The majority of experiments on membrane contactors are performed over limited time scales (typically a few days). Studies over longer time scales (e.g., months) are scarce and show that significant changes in mass transfer performance occur in some cases [77]. Membrane degradation from solvent exposure is the main reason, particularly for PP and PVDF membranes [66]. Conversely, a composite membrane with a dense skin layer has stable mass transfer performance over time, most likely due to the wetting protection effect of the dense skin layer [77].

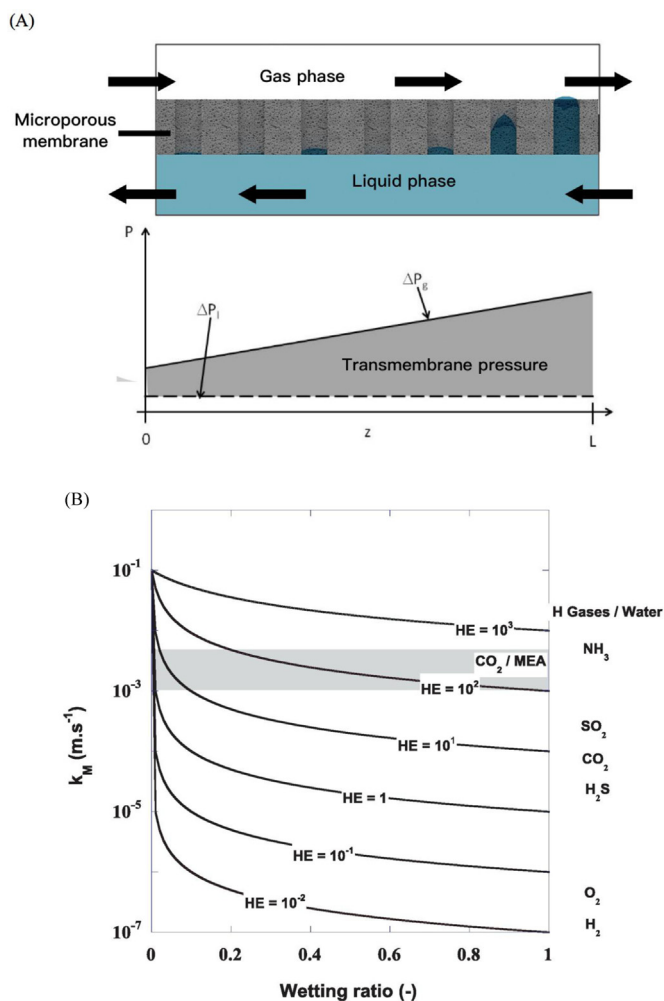Currently, no theoretical approach is available to quantitatively

Fig. 13. (A) Schematic illustration of the local wetting likely to occur in a membrane contactor under steady state operation, modified from [239]. Due to local variations in transmembrane pressure, a local wetting ratio is expected to take place. The effective overall k_m value used in simulations can thus be seen as a lumped parameter that integrates the different local mass transfer performances. (B) Influence of the wetting ratio on the effective membrane mass transfer coefficient (k_m) based on the resistance-in-series model [152]. The diffusion coefficients in the gas and liquid phases are assumed to be 10^{-5} and 10^{-9} m^2 s^{-1}, respectively. The curves correspond to different values of HE, where H is the gas–liquid Henry coefficient and E is the enhancement factor. For CO_2 absorption in MEA, HE usually varies from 100 to 300.

predict the evolution of the membrane mass transfer coefficient over time. This limitation could be seen as a major problem in membrane contactor simulation. However, time-dependent performance is also observed in other unit operations, caused by fouling (in heat exchangers and suspended liquids filtration), poisoning (in heterogeneous catalysis) or degradation (in gas–liquid absorption). Identification of the system and operating conditions that offer the most stable performance, together with an empirical expression with time evolution, is likely to be the most pragmatic answer to the tricky and hardly predictable situation.

3.6.3.4. Shell side mass transfer and fluid flow predictions. While the bore side mass transfer conditions in hollow fibers are generally estimated through consistent approaches (i.e. laminar flow of a Newtonian fluid in a smooth tube), a very broad spectrum of correlations is available for shell side mass transfer predictions. This peculiarity reflects the huge variations in terms of system structure; hollow fiber arrangement and spatial organization can significantly differ from one membrane module to another. Channeling effects, complex distribution of cross-sections depending on local bundle repartition, and turbulence promoters strongly affect the hydrodynamic conditions from one module type to another, and thus influence the mass transfer characteristics. For liquid flowing on the shell side, precisely estimating the mass transfer coefficient is a challenge, because the liquid mass transfer resistance often predominates over the resistance of the membrane and the gas phase. As a result, significant discrepancies may occur when evaluating the performance of carbon capture.

This limitation can, in principle, be overpassed when the convection diffusion approach is employed, because fluid flow conditions can be precisely taken into account in that case (e.g. Navier Stokes equation resolution). However, this requires a rigorous description of the spatial organization of the fiber packing, ideally through a 3D grid. This strategy has not been employed to date and would represent a substantial effort into module characterization through imaging techniques and computational fluid dynamics 3D simulations.

3.6.3.5. Which type of model is better for scale-up predictions? In principle, scale-up is one of the major motivations in membrane contactor simulations (Fig. 11). This point is of key importance for PCC because of the huge volume of flue gas to be treated, requiring large membrane contactors. Unfortunately, very few studies have been reported on pilot scale investigations with membrane contactors for model or real flue gas treatment [31,204]. The ability of many existing models to effectively predict the performance at a large scale is essentially unexplored. We expect that the 1D model does not offer enough prediction possibilities, due to fluid distribution peculiarities at a large scale. Pressure drop and membrane wetting effects can also complicate the prediction efficiency at large scale.

3.6.3.6. Comparison of different models. Many modeling approaches are available for membrane contactor simulations and it would be of major interest to identify the most efficient and relevant modeling strategy that best fits each of the targets (Fig. 11). The knowledge of the most adequate model complexity level, which is based on suitable simplifications in a justified manner, is a common problem in chemical engineering [208]. The situation is still not clear in membrane contactor simulation, where a broad spectrum of model complexity has been reported. Increased efforts focused on more complex developments are a recent research trend in this area. However, very few model comparison studies exist [204], which impedes a clear, systematic vision of the best use of the model portfolio summarized in Table 6.

3.6.3.7. Systematic optimization of module. The optimal design of a membrane contactor should ideally address the interplay between membrane (mass transfer coefficient), fiber (length, inner and outer diameter) and module characteristics (packing fraction, fiber spatial organization) to attain target performance in areas, such as maximal process intensification with minimal energy requirements [153]. Numerous parametric sensitivity analyses rely on one parameter, and global optimization studies are still lacking.

3.6.3.8. Beyond MEA (novel or hybrid solvents). The interest in and the potential of membrane contactors partly depend on solvent properties. Therefore, the conclusions drawn from MEA in terms of intensification performance, pressure drop limitations and energy requirements could be significantly different when a new solvent with different characteristics (e.g. kinetics, capacity, viscosity and surface tension) is employed.

Table 6
Summary of membrane contactors used for CO_2 stripping.

Membrane	Experimental conditions (e.g. absorbent-orientation; flow mode; stripping gas, and temperature)	Main remarks	Ref.
PP and PMP	Polyamidoamine dendrimer and MEA-tube side; counter-current; humidified He; ambient temperature	1. First continuous absorption-stripping system. 2. No wetting for PP-polyamidoamine system after 55 days. 3. Wetting for PMP-MEA system after 55 days (membrane resistance dominates).	[209]
Ceramic (hydrophobic)	MEA-tube side; counter-current; N_2; 80–100 °C	1. Mass transfer resistance is dominated by the liquid phase. 2. Mass transfer coefficients increase with the rise in liquid velocity. 3. Stripping efficiency improves with increasing gas velocity.	[210]
PTFE	MEA-tube side; counter-current; N_2; 90–100 °C	1. Higher liquid flow rate, temperature and liquid concentration lead to higher stripping efficiency; too high liquid concentration reduces stripping flux due to the high viscosity. 2. Gas flow rate has a minor effect on striping flux. 3. High porosity leads to high flux but also high wetting tendency.	[217]
PTFE	K_2CO_3-flatsheet; N_2; 60–100 °C	High temperature may cause wetting up to 72% of the membrane, and vapor condensation within the support layer.	[218]
PP	MEA-tube or shell side; low temperature steam; 40–70 °C	1. MEA-tube side mode achieves better performance. 2. Liquid side resistance is dominant. 3. Low vacuum improves stripper performance, but also increases pore size and thus wetting risk.	[212]
PVDF	DEA-tube side; N_2; 80–90 °C	1. Higher liquid flow rate, temperature and absorbent concentration lead to higher stripping efficiency. 2. Gas flow rate has a minor effect on stripping flux.	[238]
PSf	Water-tube side; N_2; 80 °C	1. Higher liquid flow rate and temperature lead to higher stripping efficiency. 2. Gas flow rate has a minor effect on striping flux.	[224]
PTMSP, TFC	MDEA-flatsheet; no stripping gas; 100 °C	Good stability after 250 h at temperature and pressure (i.e., 100 °C and 30 bar).	[227]
PP outside coated with fluorosiloxane	Ionic liquids with polyamidoamine dendrimer-shell side; cross flow; He, air or vacuum; 80–90 °C.	1. Continuous absorption-stripping system. 2. CO_2 transfer rates vary with different stripping methods.	[213]
PSf with SMMs	DEA and water-tube side; counter-current; N_2; 25–80 °C	Membranes spun at 15 cm air-gas have the best stripping flux.	[225]

PP: polypropylene; PMP: poly(4-methyl-2-pentyne); MEA: monoethanolamine; PTFE: polytetrafluoroethylene; PVDF: polyvinylidene fluoride; DEA: diethanolamine; PSf: polysulfone; PTMSP: poly(1-trimethylsilyl)-1-propyne; MDEA: N-methyldiethanolamine; TFC: thin-film composite; SMMs: surface modifying macromolecules.
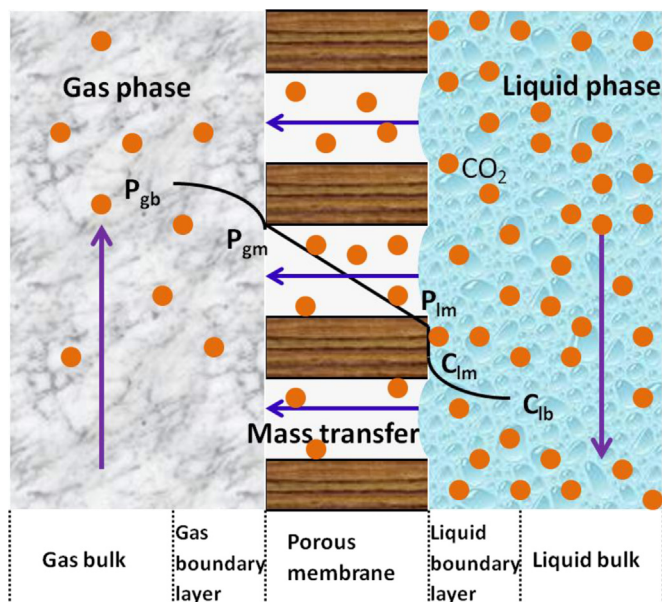

Fig. 14. Mass transfer mechanism of CO_2 from the liquid phase to the gas phase in desorption.

4. Membrane contactors in CO_2 desorption

Compared with the intensive studies on CO_2 absorption, membrane contactors have not been well developed in CO_2 desorption. In the CO_2 desorption process of PCC, gas–liquid membrane contactors can be used for direct CO_2 stripping (i.e. regeneration of liquid absorbents) and integrated heat recovery during the stripping.

4.1. CO_2 stripping

The mechanism of CO_2 desorption from the liquid absorbent through a non-wetted porous membrane (Fig. 14). Similar to the absorption process, mass transfer resistance in desorption can also be predicted by the resistance-in-series model, which considers the resistances from the membrane and gas and liquid boundary layers. However, CO_2 transfer direction is reversed from the liquid phase to the gas phase under the driving force of CO_2 partial pressure difference across the membrane.

Studies on CO_2 desorption via membrane contactors are relatively scarce, even though the desorption stage is responsible for the majority of energy consumption in PCC. One of the main reasons is that efficient CO_2 stripping generally occurs at higher temperatures that the absorption process. As a result, most polymer membranes are not stable enough under the relatively high temperatures. This reduces the technical and economic feasibility of employing polymer membrane contactors for CO_2 desorption.

Studies on membrane contactors for CO_2 stripping under different experimental conditions are summarized in Table 6. Kosaraju et al [209] were the first to employ hollow fiber membrane contactors for continuous CO_2 absorption-stripping. They reported that the issue of wetting can be successfully overcome by using a novel non-volatile amine (i.e., polyamidoamine dendrimer of generation 0) in conventional PP membrane contactors even for a long period of 55 days. However, there was no clarification in regards to the regeneration temperature, which is thought to be the ambient temperature. Similar to the selection of membrane contactors for absorption, careful selection of the membrane-absorbent combination can effectively reduce the wetting risk of the

membrane in CO_2 stripping. The first investigation on CO_2 stripping via inorganic membrane contactors was carried out in Li's group [210]. Compared with polymer membranes, inorganic membrane contactors are much more thermally and chemically stable. However, surface hydrophobic modification is essential to CO_2 desorption [210,211].

From Table 6, the following findings can be summarized:

- In most CO_2 stripping studies, N_2 is used as the stripping gas under counter-current flow.
- Compared with the temperature of a conventional desorber, the stripping temperature in membrane contactors is lower ($< 100 \, °C$). The lower regeneration temperature may allow for the use of low-grade heat (e.g., waste heat), and thus reduce the regeneration energy and cost.
- Absorbents are generally fed on the tube (i.e. lumen) side of the hollow fiber because of the better performance of this orientation [212]. However, it is reasonable to avoid this orientation when viscous absorbents (e.g. ILs) are used, due to the large friction and slow flow [213]. This orientation is more likely to lead to wetting due to pressure rise on the liquid side.
- The stripping flux and efficiency improve with increasing liquid velocity, suggesting that mass transfer resistance is dominated by the boundary layer on the liquid side.
- The stripping flux and efficiency increase slightly with the rise in gas velocity, but increase significantly with the rise in absorbent temperature, concentration and CO_2 loading.

Modeling work on CO_2 stripping is scarce. Wang et al. [214] investigated the effects of operational variables (e.g., liquid flow velocity, gas flow rate, regeneration pressure and temperature) and membrane properties (e.g., membrane length, diameter and thickness) on CO_2 desorption performance. Their model confirms that increasing liquid flow velocity and temperature improves desorption performance, and that membrane wetting can significantly deteriorate CO_2 stripping performance. They also report that reasonably increasing membrane length while reducing the diameter can improve stripping performance.

Due to the relatively low regeneration temperature in membrane contactors, stripping flux and efficiency may be sacrificed. To improve the regeneration rate, vacuum-assisted CO_2 stripping via membrane contactors has recently been investigated in Fang's group [212,215,216]. They found that better regeneration performance in terms of lower energy consumption and minimized absorbent loss can be achieved by vacuum-assisted regeneration. Although vacuum can effectively increase the regeneration rate, it also increases the risk of wetting due to the enlarged membrane pore size [212]. Therefore, more mechanically, thermally and chemically stable membranes are essential to the implementation of vacuum-assisted regeneration technology.

A number of polymer membranes have been investigated in membrane contactors for CO_2 stripping, using materials such as PP [209,212], PTFE [217,218], PVDF [82,219–223], and polysulfone (PSf) [224,225]. However, most of these membranes are tested for CO_2 desorption under moderate temperatures ($< 90 \, °C$) in short-term operation. Information on the stripping performance of polymer membranes at high temperatures in the long-term is very scarce. In practical operation, efficient stripping is generally performed at elevated temperatures and pressures in the desorber, which makes most polymeric membranes unsuitable for contactor applications.

Recently, some efforts have made to develop more thermally and chemically robust membranes for CO_2 stripping. Trusov et al. [226] fabricated dense membranes with hydrophobic glass polymers with high free volume, such as PTMSP, poly[1-(tri-methylgermil)-1-propyne] (PTMGP) and PMP. These dense
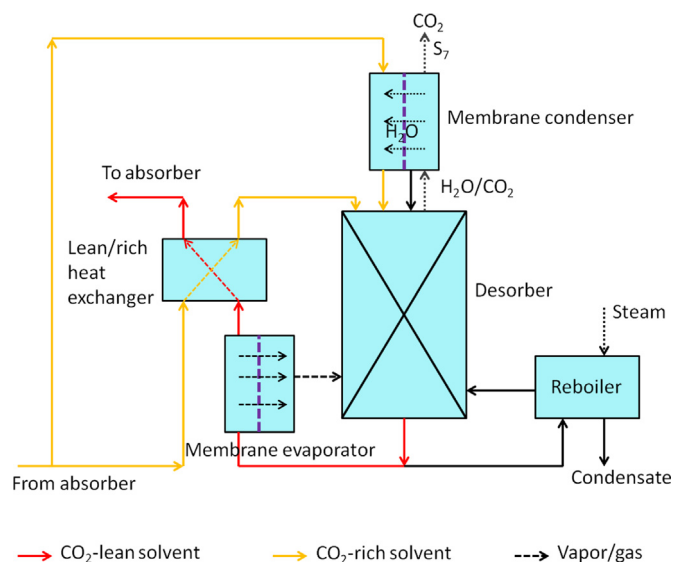

Fig. 15. Schematic diagram of the Membrane Assisted Liquid Absorbent Regeneration (MALAR) system [58].

membranes show excellent long-term stabilities with various absorbents under high temperature and pressure, offering great promise for CO_2 stripping by pressure and temperature swing in membrane contactors. More recently, the same group developed thin film composite PTMSP membranes for desorption by a novel two-layer coating technique [227]. The prepared membranes have good, stable regeneration behaviors at high temperature ($100 \, °C$) and pressure ($30 \, bar$) in 100-h test. The group also fabricated another robust glass polymer membrane for CO_2 stripping via membrane contactors poly[bis(trimethylsilyl)tricyclononene] (PBTMST), which has a T_g ($\geq 370 \, °C$) [228].

Practical CO_2 stripping requires membranes with excellent mechanical, thermal and chemical stabilities for use in the contactors. Several strategies can be employed to develop such membranes, such as

i. hydrophobic modification of inorganic membrane surfaces [211],
ii. selection of polymers with high T_g and CO_2 permeabilities [226–228],
iii. incorporation of hydrophobic macromolecule [222,225],
iv. surface modification using novel polymers [213],
v. careful selection of membrane-absorbent combination [209,213],
vi. development of hybrid organic–inorganic membranes [229,230].

Relevant studies on robust membrane development for CO_2 stripping in membrane contactors are still rare, and this area needs more attention in the future.

4.2. Integrated heat recovery

In addition to direct CO_2 stripping, gas–liquid membrane contactors can also be used for heat recovery in the desorption process. A novel membrane assisted liquid absorbent regeneration (MALAR) process that employs gas–liquid membrane contactors for latent heat recovery in desorption has been investigated [58,231]. The process concept is schematically illustrated in Fig. 15. The MALAR system has two gas–liquid membrane contactors: one as the membrane condenser on top of the desorber, and the other one as the membrane evaporator at the bottom of desorber. The

membrane condenser aims to recover the latent heat within the water vapor saturated CO_2 stream exiting from the desorber. In the membrane condenser, one side of the membrane is a high temperature gas stream and the other side is a low temperature liquid stream (i.e., absorbent bypass). The membrane evaporator aims to transfer partial heat from the hot lean absorbent back to the desorber, thus improving the energy efficiency of the system. In the membrane evaporator, a high temperature liquid stream is on one side of the membrane, while low temperature gas stream is on the other side. In these gas–liquid membrane contactors (i.e., membrane condenser and membrane evaporator), the driving force for mass transfer is the water vapor partial pressure difference across the membrane.

Theoretical thermodynamic analysis of mass and heat transfer in the membrane condensation system (i.e., membrane condenser) has been recently carried out [232]. The study reveals that the optimal split mass flow rate is determined by the inlet gas temperature and the overall heat-transfer coefficient of the membrane. The required membrane area is strongly dependent on the overall heat-transfer coefficient, particularly at higher inlet gas temperatures. It is also found that mass transfer across the membrane has an insignificant effect on heat transfer and heat recovery, suggesting that membrane wetting (the major issue in conventional membrane contactors) may not become an issue in the membrane condenser.

Zhao et al. [58] experimentally investigated the effects of operational parameters on mass and heat transfer in the membrane evaporator. They report that vapor and heat fluxes increase significantly with the rise in evaporation temperature and gas flow rate, and that the liquid flow rate has a minor effect on the mass and heat transfer. This suggests that the mass transfer resistance in the membrane evaporator is dominated by the boundary layer on the gas side, which is contrary to the dominant mass transfer resistance in membrane contactors for CO_2 stripping as discussed in Section 4.1. Similar to the membrane contactors for CO_2 stripping, a sweep gas or vacuum on the permeate side can be applied in the membrane evaporator application as long as there is sufficient water vapor partial pressure gradient across the membrane as the driving force.

Both theoretical and experimental studies show that gas–liquid membrane contactors (e.g., membrane condenser and membrane evaporator) offer great promise for heat integration in CO_2 desorption [58]. However, more thermally and chemically robust membranes are needed for the higher working temperature compared with the absorption temperature. Inorganic membranes with high heat transfer coefficients can be good candidates for such integrated heat recovery [232].

5. Concluding remarks and recommendations

This review offers a state-of-the-art assessment of the research work carried out to date on membrane contactors in PCC. As a promising technology, the membrane contactor has attracted considerable interest for CO_2 capture, principally because it integrates the benefits of both liquid absorption (high selectivity) and membrane separation (modularity and compactness). Most research on membrane contactors CO_2 capture is still conducted at the laboratory scale, because of the critical challenge from membrane wetting. Even slight wetting can significantly increase the mass transfer resistance, reducing CO_2 absorption performance. To successfully minimize membrane wetting, a better understanding of the interactions between membranes and absorbents, as well as the developments of both new membranes and novel green solvents, is required. Membrane contactors with non-porous membranes have been a new research direction in recent years. Novel

solvents with desirable physicochemical characteristics (e.g., low viscosity and fast reaction kinetics) for CO_2 capture via membrane contactors should be further explored. The conditions that make membrane contactors more attractive than conventional absorption technology are not clearly defined yet, and more efforts should be made into this aspect.

In practical industrial scale demonstrations, to maintain sufficient and stable absorption performance in long-term operations, hollow fiber membrane contactor modules with more robust membrane materials (e.g., PTFE, PEEK, fluorinated polyamides and inorganic ones) should be developed. With more thermally and chemically stable membrane modules, CO_2 absorption performance over a long timescale (e.g., years) at large pilot or industrial scales should be fully studied before this membrane-based absorption technology can be commercialized. In laboratory scale membrane contactor studies, recent attention has been paid to integration of new materials (e.g., enzymes and nanoparticles) on or in the membranes, and combination of novel green solvents (e.g., ILs and amino acid salts).

Apart from high performance membrane materials, search for better module geometries could also be of interest. Mass transfer resistance from the liquid phase is often dominant in gas absorption with membrane contactors. Optimizing fluid flow conditions, beyond the fiber array solution (hollow fiber module) and providing turbulence promotion with a minimal supplementary energy requirement, can increase the overall module productivity. Optimal geometries can offer efficient heat and mass transfer performance in the system, but relevant investigations remain largely unexplored to date.

Most studies on membrane contactors are still focused on CO_2 absorption, and very limited research on their applications in the solvent regeneration process has been carried out so far, although membrane contactors have shown potential in both direct CO_2 stripping and integrated heat recovery. In the future, more efforts (including both lab-scale investigations and pilot-scale demonstrations) should be made to study the applications of membrane contactors in the regeneration process since this process principally determines the energy consumption and thus costs of PCC. The pilot plant activities conducted thus far indicate the technological viability of the membrane contactor concept for CO_2 capture. Work is continuing to translate this experience into a commercial membrane product.

Nomenclature

a	interfacial area ($m^2\,m^{-3}$)
B	pore geometry coefficient (dimensionless)
C	concentration ($mol\,m^{-3}$)
d	diameter (m)
D	diffusion coefficient ($m^2\,s^{-1}$)
E	enhancement factor (dimensionless)
H	Henry's Law constant
Ha	Hatta number (dimensionless)
k	individual mass transfer coefficient ($m\,s^{-1}$)
K	overall mass transfer coefficient ($m\,s^{-1}$)
kr	kinetic constant ($m^3\,mol^{-1}\,s^{-1}$)
L	effective module length (m)
m	gas–liquid partition coefficient (dimensionless)
M	molar mass ($kg\,mol^{-1}$)
N	molar flux ($mol\,m^{-2}\,s^{-1}$)
P	pressure (Pa)
r	distance in radial direction from the fiber axis; radius (m)

R_{CO2}	CO_2 absorption rate per unit volume of the contactor (mol m^{-3} s^{-1})
Sh	Sherwood number (dimensionless)
T	temperature (K)
u	velocity (m s^{-1})
v	interstitial fluid velocity (m s^{-1})

Subscripts

b	bulk
e	external
g	gas
i	component i; inner
o	outer
l	liquid
ln	logarithmic mean
m	membrane
z	axial coordinate (m)

Greek symbols

ε	membrane porosity (dimensionless)
δ	membrane thickness (m)
τ	membrane tortuosity (dimensionless)
ρ	density (kg m^{-3})
γ	liquid surface tension (dynes cm^{-1})
θ	contact angle
η	CO_2 capture ratio (dimensionless)

References

[1] K.M.K. Yu, I. Curcic, J. Gabriel, S.C.E. Tsang, Recent advances in CO_2 capture and utilization, ChemSusChem 1 (2008) 893–899.

[2] M. Wang, A. Lawal, P. Stephenson, J. Sidders, C. Ramshaw, Post-combustion CO_2 capture with chemical absorption: a state-of-the-art review, Chem. Eng. Res. Des. 89 (2011) 1609–1624.

[3] A. Neftel, E. Moor, H. Oeschger, B. Stauffer, Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries, Nature 315 (1985) 45–47.

[4] P. Freund, Making deep reductions in CO_2 emissions from coal-fired power plant using capture and storage of CO_2. In: Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy, 217, 2003, pp. 1–7.

[5] D.M. D'Alessandro, B. Smit, J.R. Long, Carbon dioxide capture: prospects for new materials, Angew. Chem. Int. Ed. 49 (2010) 6058–6082.

[6] J.D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, R.D. Srivastava, Advances in CO_2 capture technology – the U.S. Department of Energy's Carbon Sequestration Program, Int. J. Greenh. Gas Control 2 (2008) 9–20.

[7] P.H.M. Feron, Exploring the potential for improvement of the energy performance of coal fired power plants with post-combustion capture of carbon dioxide, Int. J. Greenh. Gas Control 4 (2010) 152–160.

[8] A.L. Kohl, R.B. Nielsen, Gas Purification, Fifth Ed., Gulf Professional Publishing, Houston, 1997.

[9] R. Perry, D.W. Green, Perry's Chemical Engineers' Handbook, McGraw-Hill, United States, 2007.

[10] A. Gabelman, S.-T. Hwang, Hollow fiber membrane contactors, J. Membr. Sci. 159 (1999) 61–106.

[11] M. Mavroudi, S.P. Kaldis, G.P. Sakellaropoulos, Reduction of CO_2 emissions by a membrane contacting process, Fuel 82 (2003) 2153–2159.

[12] V.Y. Dindore, D.W.F. Brilman, G.F. Versteeg, Hollow fiber membrane contactor as a gas–liquid model contactor, Chem. Eng. Sci. 60 (2005) 467–479.

[13] R. Klaassen, P.H.M. Feron, A.E. Jansen, Membrane contactors in industrial applications, Chem. Eng. Res. Des. 83 (2005) 234–246.

[14] Z. Qi, E.L. Cussler, Microporous hollow fibers for gas absorption: I. Mass transfer in the liquid, J. Membr. Sci. 23 (1985) 321–332.

[15] Z. Qi, E.L. Cussler, Microporous hollow fibers for gas absorption: II. Mass transfer across the membrane, J. Membr. Sci. 23 (1985) 333–345.

[16] H.H. Park, B.R. Deshwal, I.W. Kim, H.K. Lee, Absorption of SO_2 from flue gas using PVDF hollow fiber membranes in a gas–liquid contactor, J. Membr. Sci. 319 (2008) 29–37.

[17] K. Li, D. Wang, C.C. Koe, W.K. Teo, Use of asymmetric hollow fibre modules for elimination of H_2S from gas streams via a membrane absorption method, Chem. Eng. Sci. 53 (1998) 1111–1119.

[18] T.K. Poddar, S. Majumdar, K.K. Sirkar, Membrane-based absorption of VOCs from a gas stream, AIChE J. 42 (1996) 3267–3282.

[19] J.-L. Li, B.-H. Chen, Review of CO_2 absorption using chemical solvents in hollow fiber membrane contactors, Sep. Purif. Technol. 41 (2005) 109–122.

[20] A. Mansourizadeh, A.F. Ismail, Hollow fiber gas–liquid membrane contactors for acid gas capture: a review, J. Hazard. Mater. 171 (2009) 38–53.

[21] Z. Cui, D. deMontigny, Part 7: a review of CO_2 capture using hollow fiber membrane contactors, Carbon Manag. 4 (2013) 69–89.

[22] E. Drioli, A.I. Stankiewicz, F. Macedonio, Membrane engineering in process intensification – an overview, J. Membr. Sci. 380 (2011) 1–8.

[23] O. Falk-Pedersen, M.S. Grønvold, P. Nøkleby, F. Bjerve, H.F. Svendsen, CO_2 capture with membrane contactors, Int. J. Green Energy 2 (2005) 157–165.

[24] D. deMontigny, P. Tontiwachwuthikul, A. Chakma, Comparing the absorption performance of packed columns and membrane contactors, Ind. Eng. Chem. Res. 44 (2005) 5726–5732.

[25] P.H.M. Feron, A.E. Jansen, Capture of carbon dioxide using membrane gas absorption and reuse in the horticultural industry, Energy Convers. Manag. 36 (1995) 411–414.

[26] R. Klaassen, P. Feron, A. Jansen, Membrane contactor applications, Desalination 224 (2008) 81–87.

[27] P.H.M. Feron, A.E. Jansen, R. Klaassen, Membrane technology in carbon dioxide removal, Energy Convers. Manag. 33 (1992) 421–428.

[28] O. Falk-Pedersen, Y. Bjerve, G. Glittum, S. Rønning, Separation of carbon dioxide from offshore gas turbine exhaust, Energy Convers. Manag. 36 (1995) 393–396.

[29] O. Falk-Pedersen, H. Dannström, Separation of carbon dioxide from offshore gas turbine exhaust, Energy Conver. Manag. 38 (Supplement) (1997) S81–S86.

[30] M. Søbye Grønvold, O. Falk-Pedersen, N. Imai, K. Ishida, KPS membrane contactor module combined with Kansai/MHI advanced solvent, KS-1 for CO_2 seperation from combustion flue gases, in: D.C. Thomas, S.M. Benson (Eds.), Carbon Dioxide Capture for Storage in Deep Geologic Formations, Advanced Resources International Inc., USA, 2005.

[31] N. Nishikawa, M. Ishibashi, H. Ohta, N. Akutsu, H. Matsumoto, T. Kamata, H. Kitamura, CO_2 removal by hollow-fiber gas–liquid contactor, Energy Convers. Manag. 36 (1995) 415–418.

[32] A.E. Jansen, R. Klaassen, P.H.M. Feron, J.H. Hanemaaijer, B. Meulen, Membrane gas absorption processes in environmental applications, in: J.G. Crespo, K.W. Böddeker (Eds.), Membrane Processes in Separation and Purification, Springer Netherlands, Dordrecht, 1994, pp. 343–356.

[33] R. Klaassen, Achieving flue gas desulphurization with membrane gas absorption, Filtr. Sep. 40 (2003) 26–28.

[34] R. Klaassen, A.E. Jansen, The membrane contactor: environmental applications and possibilities, Environ. Progress 20 (2001) 37–43.

[35] P.H.M. Feron, A.E. Jansen, CO_2 separation with polyolefin membrane contactors and dedicated absorption liquids: performances and prospects, Sep. Purif. Technol. 27 (2002) 231–242.

[36] A. Qader, Demonstrating carbon capture, TCE: The Chemical Engineer, 2009, pp. 30–31.

[37] C.A. Scholes, A. Qader, G.W. Stevens, S.E. Kentish, Membrane gas-solvent contactor pilot plant trials of CO_2 absorption from flue gas, Sep. Sci. Technol. 49 (2014) 2449–2458.

[38] S.J. Zhou, H.S. Meyer, B. Bikson, Y. Ding, Hybrid Membrane Absorption Process for Post Combustion CO_2 Capture, 2010 Spring Meeting & 6th Global Congress on Process Safety, AIChE, San Antonio, Texas, 2010.

[39] S. Li, D.J. Rocha, S. James Zhou, H.S. Meyer, B. Bikson, Y. Ding, Post-combustion CO_2 capture using super-hydrophobic, polyether ether ketone, hollow fiber membrane contactors, J. Membr. Sci. 430 (2013) 79–86.

[40] S. Li, J. Zhou, T. Pyrzynski, A. Makkuni, H. Meyer, Y. Ding, B. Bikson, Hybrid Membrane/Absorption Process for Post-combustion CO_2 Capture, Final Technical Report, in, 2014.

[41] H. Herzog, O. Falk-Pedersen, The Kvaerner membrane contactor: lessons from a case study in how to reduce carpture costs, in: Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies. Cairns, Australia, 2000.

[42] C.A. Scholes, M. Simioni, A. Qader, G.W. Stevens, S.E. Kentish, Membrane gas-solvent contactor trials of CO_2 absorption from syngas, Chem. Eng. J. 195–196 (2012) 188–197.

[43] E. Favre, Membrane processes and postcombustion carbon dioxide capture: challenges and prospects, Chem. Eng. J. 171 (2011) 782–793.

[44] F. Wiesler, Membrane contactors: an introduction to the technology, Ultrapure Water, May 1996, pp. 27–31.

[45] W.S.W. Ho, K.K. Sirkar, Membrane Handbook, Springer Science+Business Media, New York, US, 1992.

[46] M. Mavroudi, S.P. Kaldis, G.P. Sakellaropoulos, A study of mass transfer resistance in membrane gas–liquid contacting processes, J. Membr. Sci. 272 (2006) 103–115.

[47] S. Khaisri, D. deMontigny, P. Tontiwachwuthikul, R. Jiraratananon, Comparing membrane resistance and absorption performance of three different membranes in a gas absorption membrane contactor, Sep. Purif. Technol. 65 (2009) 290–297.

[48] S.-H. Lin, C.-F. Hsieh, M.-H. Li, K.-L. Tung, Determination of mass transfer resistance during absorption of carbon dioxide by mixed absorbents in PVDF and PP membrane contactor, Desalination 249 (2009) 647–653.

[49] S. Atchariyawut, C. Feng, R. Wang, R. Jiraratananon, D.T. Liang, Effect of membrane structure on mass-transfer in the membrane gas–liquid contacting process using microporous PVDF hollow fibers, J. Membr. Sci. 285 (2006) 272–281.

[50] A. Mansourizadeh, A.F. Ismail, T. Matsuura, Effect of operating conditions on the physical and chemical CO_2 absorption through the PVDF hollow fiber membrane contactor, J. Membr. Sci. 353 (2010) 192–200.

[51] S. Mosadegh-Sedghi, D. Rodrigue, J. Brisson, M.C. Iliuta, Wetting phenomenon in membrane contactors – causes and prevention, J. Membr. Sci. 452 (2014) 332–353.

[52] H.A. Rangwala, Absorption of carbon dioxide into aqueous solutions using hollow fiber membrane contactors, J. Membr. Sci. 112 (1996) 229–240.

[53] Lu, Wang, Sun, Li, Liu, Absorption of CO_2 into aqueous solutions of methyldiethanolamine and activated methyldiethanolamine from a gas mixture in a hollow fiber contactor, Ind. Eng. Chem. Res. 44 (2005) 9230–9238.

[54] H.-Y. Zhang, R. Wang, D.T. Liang, J.H. Tay, Theoretical and experimental studies of membrane wetting in the membrane gas–liquid contacting process for CO_2 absorption, J. Membr. Sci. 308 (2008) 162–170.

[55] H. Kreulen, C.A. Smolders, G.F. Versteeg, W.P.M. Van Swaaij, Microporous hollow

fibre membrane modules as gas–liquid contractors. Part 2. Mass transfer with chemical reaction, J. Membr. Sci. 78 (1993) 217–238.

[56] R. Wang, H.Y. Zhang, P.H.M. Feron, D.T. Liang, Influence of membrane wetting on CO_2 capture in microporous hollow fiber membrane contactors, Sep. Purif. Technol. 46 (2005) 33–40.

[57] S. Zhao, P.H.M. Feron, C. Cao, L. Wardhaugh, S. Yan, S. Gray, Membrane evaporation of amine solution for energy saving in post-combustion carbon capture: wetting and condensation, Sep. Purif. Technol. 146 (2015) 60–67.

[58] S. Zhao, C. Cao, L. Wardhaugh, P.H.M. Feron, Membrane evaporation of amine solution for energy saving in post-combustion carbon capture: performance evaluation, J. Membr. Sci. 473 (2015) 274–282.

[59] P.S. Kumar, J.A. Hogendoorn, P.H.M. Feron, G.F. Versteeg, New absorption liquids for the removal of CO_2 from dilute gas streams using membrane contactors, Chem. Eng. Sci. 57 (2002) 1639–1651.

[60] A.C.M. Franken, J.A.M. Nolten, M.H.V. Mulder, D. Bargeman, C.A. Smolders, Wetting criteria for the applicability of membrane distillation, J. Membr. Sci. 33 (1987) 315–328.

[61] K.S. McGuire, K.W. Lawson, D.R. Lloyd, Pore size distribution determination from liquid permeation through microporous membranes, J. Membr. Sci. 99 (1995) 127–137.

[62] J.-G. Lu, Y.-F. Zheng, M.-D. Cheng, Wetting mechanism in mass transfer process of hydrophobic membrane gas absorption, J. Membr. Sci. 308 (2008) 180–190.

[63] Y. Lv, X. Yu, S.-T. Tu, J. Yan, E. Dahlquist, Wetting of polypropylene hollow fiber membrane contactors, J. Membr. Sci. 362 (2010) 444–452.

[64] L. Zhang, R. Qu, Y. Sha, X. Wang, L. Yang, Membrane gas absorption for CO_2 capture from flue gas containing fine particles and gaseous contaminants, Int. J. Greenh. Gas Control 33 (2015) 10–17.

[65] X. Wang, H. Chen, L. Zhang, R. Yu, R. Qu, L. Yang, Effects of coexistent gaseous components and fine particles in the flue gas on CO_2 separation by flat-sheet polysulfone membranes, J. Membr. Sci. 470 (2014) 237–245.

[66] R. Wang, D.F. Li, C. Zhou, M. Liu, D.T. Liang, Impact of DEA solutions with and without CO_2 loading on porous polypropylene membranes intended for use as contactors, J. Membr. Sci. 229 (2004) 147–157.

[67] A.M. Barbe, P.A. Hogan, R.A. Johnson, Surface morphology changes during initial usage of hydrophobic, microporous polypropylene membranes, J. Membr. Sci. 172 (2000) 149–156.

[68] C. Saiwan, T. Supap, R.O. Idem, P. Tontiwachwuthikul, Part 3: corrosion and prevention in post-combustion CO_2 capture systems, Carbon Manag. 2 (2011) 659–675.

[69] N. Kladkaew, R. Idem, P. Tontiwachwuthikul, C. Saiwan, Studies on corrosion and corrosion inhibitors for amine based solvents for CO_2 absorption from power plant flue gases containing CO_2, O_2 and SO_2, Energy Procedia 4 (2011) 1761–1768.

[70] D. deMontigny, P. Tontiwachwuthikul, A. Chakma, Using polypropylene and polytetrafluoroethylene membranes in a membrane contactor for CO_2 absorption, J. Membr. Sci. 277 (2006) 99–107.

[71] S.-H. Lin, K.-L. Tung, W.-J. Chen, H.-W. Chang, Absorption of carbon dioxide by mixed piperazine-alkanolamine absorbent in a plasma-modified polypropylene hollow fiber contactor, J. Membr. Sci. 333 (2009) 30–37.

[72] A. Xu, A. Yang, S. Young, D. deMontigny, P. Tontiwachwuthikul, Effect of internal coagulant on effectiveness of polyvinylidene fluoride membrane for carbon dioxide separation and absorption, J. Membr. Sci. 311 (2008) 153–158.

[73] A. Mansourizadeh, A.F. Ismail, Effect of LiCl concentration in the polymer dope on the structure and performance of hydrophobic PVDF hollow fiber membranes for CO_2 absorption, Chem. Eng. J. 165 (2010) 980–988.

[74] C. Feng, R. Wang, H. Zhang, L. Shi, Diverse morphologies of PVDF hollow fiber membranes and their performance analysis as gas/liquid contactors, J. Appl. Polym. Sci. 119 (2011) 1259–1267.

[75] A. Mansourizadeh, A.F. Ismail, A developed asymmetric PVDF hollow fiber membrane structure for CO_2 absorption, Int. J. Greenh. Gas Control 5 (2011) 374–380.

[76] S.-C. Chen, S.-H. Lin, R.-D. Chien, P.-S. Hsu, Effects of shape, porosity, and operating parameters on carbon dioxide recovery in polytetrafluoroethylene membranes, J. Hazard. Mater. 179 (2010) 692–700.

[77] E. Chabanon, D. Roizard, E. Favre, Membrane contactors for postcombustion carbon dioxide capture: a comparative study of wetting resistance on long time scales, Ind. Eng. Chem. Res. 50 (2011) 8237–8244.

[78] K.A. Hoff, O. Juliussen, O. Falk-Pedersen, H.F. Svendsen, Modeling and experimental study of carbon dioxide absorption in aqueous alkanolamine solutions using a membrane contactor, Ind. Eng. Chem. Res. 43 (2004) 4908–4921.

[79] S. Mosadegh-Sedghi, J. Brisson, D. Rodrigue, M.C. Iliuta, Morphological, chemical and thermal stability of microporous LDPE hollow fiber membranes in contact with single and mixed amine based CO_2 absorbents, Sep. Purif. Technol. 96 (2012) 117–123.

[80] S.M. Sedghi, J. Brisson, D. Rodrigue, M.C. Iliuta, Chemical alteration of LDPE hollow fibers exposed to monoethanolamine solutions used as absorbent for CO_2 capture process, Sep. Purif. Technol. 80 (2011) 338–344.

[81] S. Li, S.J. Zhou, T. Pyrzynski, H. Meyer, Y. Ding, B. Bikson, Post-combustion CO_2 capture using PEEK hollow fiber membrane contactors, in: Proceedings of the 10th International Congress on Membranes and Membrane Processes, Suzhou, China, 2014.

[82] R. Naim, A.F. Ismail, A. Mansourizadeh, Effect of non-solvent additives on the structure and performance of PVDF hollow fiber membrane contactor for CO_2 stripping, J. Membr. Sci. 423–424 (2012) 503–513.

[83] A. Mansourizadeh, A.F. Ismail, M.S. Abdullah, B.C. Ng, Preparation of polyvinylidene fluoride hollow fiber membranes for CO_2 absorption using phase-inversion promoter additives, J. Membr. Sci. 355 (2010) 200–207.

[84] A. Mansourizadeh, A.F. Ismail, Preparation and characterization of porous PVDF hollow fiber membranes for CO_2 absorption: effect of different non-solvent additives in the polymer dope, Int. J. Greenh. Gas Control 5 (2011) 640–648.

[85] N. Ghasem, M. Al-Marzouqi, L. Zhu, Preparation and properties of polyethersulfone hollow fiber membranes with o-xylene as an additive used in membrane contactors for CO_2 absorption, Sep. Purif. Technol. 92 (2012) 1–10.

[86] M. Rahbari-Sisakht, A.F. Ismail, D. Rana, T. Matsuura, A novel surface modified polyvinylidene fluoride hollow fiber membrane contactor for CO_2 absorption, J.

[87] A. Mansourizadeh, Z. Aslmahdavi, A.F. Ismail, T. Matsuura, Blend polyvinylidene fluoride/surface modifying macromolecule hollow fiber membrane contactors for CO_2 absorption, Int. J. Greenh. Gas Control 26 (2014) 83–92.

[88] N. Ghasem, M. Al-Marzouqi, A. Duidar, Effect of PVDF concentration on the morphology and performance of hollow fiber membrane employed as gas–liquid membrane contactor for CO_2 absorption, Sep. Purif. Technol. 98 (2012) 174–185.

[89] S.P. Deshmukh, K. Li, Effect of ethanol composition in water coagulation bath on morphology of PVDF hollow fibre membranes, J. Membr. Sci. 150 (1998) 75–85.

[90] N. Ghasem, M. Al-Marzouqi, A. Duaidar, Effect of quenching temperature on the performance of poly(vinylidene fluoride) microporous hollow fiber membranes fabricated via thermally induced phase separation technique on the removal of CO_2 from CO_2-gas mixture, Int. J. Greenh. Gas Control 5 (2011) 1550–1558.

[91] N. Ghasem, M. Al-Marzouqi, N. Abdul Rahim, Effect of polymer extrusion temperature on poly(vinylidene fluoride) hollow fiber membranes: properties and performance used as gas–liquid membrane contactor for CO_2 absorption, Sep. Purification Technol. 99 (2012) 91–103.

[92] F. Korminouri, M. Rahbari-Sisakht, D. Rana, T. Matsuura, A.F. Ismail, Study on the effect of air-gap length on properties and performance of surface modified PVDF hollow fiber membrane contactor for carbon dioxide absorption, Sep. Purif. Technol. 132 (2014) 601–609.

[93] F. Korminouri, M. Rahbari-Sisakht, T. Matsuura, A.F. Ismail, Surface modification of polysulfone hollow fiber membrane spun under different air-gap lengths for carbon dioxide absorption in membrane contactor system, Chem. Eng. J. 264 (2015) 453–461.

[94] S.A. Stern, V.M. Shah, B.J. Hardy, Structure-permeability relationships in silicone polymers, J. Polym. Sci. Part B: Polym. Phys. 25 (1987) 1263–1298.

[95] Y. Ichiraku, S.A. Stern, T. Nakagawa, An investigation of the high gas permeability of poly (1-trimethylsilyl-1-propyne), J. Membr. Sci. 34 (1987) 5–18.

[96] J.C. Lötters, W. Olthuis, P.H. Veltink, P. Bergveld, The mechanical properties of the rubber elastic polymer polydimethylsiloxane for sensor applications, J. Micromech. Microeng. 7 (1997) 145.

[97] K. Kneifel, S. Nowak, W. Albrecht, R. Hilke, R. Just, K.V. Peinemann, Hollow fiber membrane contactor for air humidity control: modules and membranes, J. Membr. Sci. 276 (2006) 241–251.

[98] K. Li, W.K. Teo, An ultrathin skinned hollow fibre module for gas absorption at elevated pressures, Chem. Eng. Res. Des. 74 (1996) 856–862.

[99] D.G. Bessarabov, R.D. Sanderson, E.P. Jacobs, I.N. Beckman, High-efficiency separation of an ethylene/ethane mixture by a large-scale liquid-membrane contactor containing flat-sheet nonporous polymeric gas-separation membranes and a selective flowing-liquid absorbent, Ind. Eng. Chem. Res. 34 (1995) 1769–1778.

[100] D.C. Nymeijer, B. Folkers, I. Breebaart, M.H.V. Mulder, M. Wessling, Selection of top layer materials for gas–liquid membrane contactors, J. Appl. Polym. Sci. 92 (2004) 323–334.

[101] W. Albrecht, R. Hilke, K. Kneifel, T. Weigel, K.V. Peinemann, Selection of microporous hydrophobic membranes for use in gas/liquid contactors: an experimental approach, J. Membr. Sci. 263 (2005) 66–76.

[102] S. Heile, S. Rosenberger, A. Parker, B. Jefferson, E.J. McAdam, Establishing the suitability of symmetric ultrathin wall polydimethylsiloxane hollow-fibre membrane contactors for enhanced CO_2 separation during biogas upgrading, J. Membr. Sci. 452 (2014) 37–45.

[103] K. Li, W.K. Teo, Use of permeation and absorption methods for CO_2 removal in hollow fibre membrane modules, Sep. Purif. Technol. 13 (1998) 79–88.

[104] H.B. Al-saffar, B. Ozturk, R. Hughes, A comparison of porous and non-porous gas–liquid membrane contactors for gas separation, Chem. Eng. Res. Des. 75 (1997) 685–692.

[105] A. McLeod, P. Buzatu, O. Autin, B. Jefferson, E. McAdam, Controlling shell-side crystal nucleation in a gas–liquid membrane contactor for simultaneous ammonium bicarbonate recovery and biogas upgrading, J. Membr. Sci. 473 (2015) 146–156.

[106] P.T. Nguyen, E. Lasseuguette, Y. Medina-Gonzalez, J.C. Remigy, D. Roizard, E. Favre, A dense membrane contactor for intensified CO_2 gas/liquid absorption in post-combustion capture, J. Membr. Sci. 377 (2011) 261–272.

[107] Y. Zhang, R. Wang, Novel method for incorporating hydrophobic silica nanoparticles on polyetherimide hollow fiber membranes for CO_2 absorption in a gas–liquid membrane contactor, J. Membr. Sci. 452 (2014) 379–389.

[108] Y. Zhang, R. Wang, Fabrication of novel polyetherimide-fluorinated silica organic–inorganic composite hollow fiber membranes intended for membrane contactor application, J. Membr. Sci. 443 (2013) 170–180.

[109] M. Rezaei, A.F. Ismail, G. Bakeri, S.A. Hashemifard, T. Matsuura, Effect of general montmorillonite and Cloisite 15A on structural parameters and performance of mixed matrix membranes contactor for CO_2 absorption, Chem. Eng. J. 260 (2015) 875–885.

[110] M. Rezaei, A.F. Ismail, S.A. Hashemifard, G. Bakeri, T. Matsuura, Experimental study on the performance and long-term stability of PVDF/montmorillonite hollow fiber mixed matrix membranes for CO_2 separation process, Int. J. Greenh. Gas Control 26 (2014) 147–157.

[111] M.E. Russo, G. Olivieri, A. Marzocchella, P. Salatino, P. Caramuscio, C. Cavaleiro, Post-combustion carbon capture mediated by carbonic anhydrase, Sep. Purif. Technol. 107 (2013) 331–339.

[112] J.K.J. Yong, G.W. Stevens, F. Caruso, S.E. Kentish, The use of carbonic anhydrase to accelerate carbon dioxide capture processes, J. Chem. Technol. Biotechnol. 90 (2015) 3–10.

[113] L.-H. Cheng, L. Zhang, H.-L. Chen, C.-J. Gao, Hollow fiber contained hydrogel-CA membrane contactor for carbon dioxide removal from the enclosed spaces, J. Membr. Sci. 324 (2008) 33–43.

[114] E. Ozdemir, Biomimetic CO_2 sequestration: 1. immobilization of carbonic anhydrase within polyurethane foam, Energy Fuels 23 (2009) 5725–5730.

[115] Y.-T. Zhang, L. Zhang, H.-L. Chen, H.-M. Zhang, Selective separation of low concentration CO_2 using hydrogel immobilized CA enzyme based hollow fiber membrane reactors, Chem. Eng. Sci. 65 (2010) 3199–3207.

[116] J. Hou, G. Dong, B. Xiao, C. Malassigne, V. Chen, Preparation of titania based biocatalytic nanoparticles and membranes for CO_2 conversion, J. Mater. Chem. A 3

(2015) 3332–3342.

[117] R.G. Khalifah, The carbon dioxide hydration activity of carbonic anhydrase: I. Stop-flow kinetic studies on the native human isoenzymes B and C, J. Biol. Chem. 246 (1971) 2561–2573.

[118] B.C. Tripp, K. Smith, J.G. Ferry, Carbonic anhydrase: new insights for an ancient enzyme, J. Biol. Chem. 276 (2001) 48615–48618.

[119] R.M. Cowan, J.J. Ge, Y.J. Qin, M.L. McGregor, M.C. Trachtenberg, CO$_2$ capture by means of an enzyme-based reactor, Ann. N.Y. Acad. Sci. 984 (2003) 453–469.

[120] T. Enns, Facilitation by carbonic anhydrase of carbon dioxide transport, Science 155 (1967) 44–47.

[121] L. Bao, M.C. Trachtenberg, Facilitated transport of CO$_2$ across a liquid membrane: comparing enzyme, amine, and alkaline, J. Membr. Sci. 280 (2006) 330–334.

[122] J. Luo, F. Marpani, R. Brites, L. Frederiksen, A.S. Meyer, G. Jonsson, M. Pinelo, Directing filtration to optimize enzyme immobilization in reactive membranes, J. Membr. Sci. 459 (2014) 1–11.

[123] J. Luo, A.S. Meyer, G. Jonsson, M. Pinelo, Enzyme immobilization by fouling in ultrafiltration membranes: impact of membrane configuration and type on flux behavior and biocatalytic conversion efficacy, Biochem. Eng. J. 83 (2014) 79–89.

[124] L. Giorno, E. Drioli, G. Carvoli, A. Cassano, L. Donato, Study of an enzyme membrane reactor with immobilized fumarase for production of L-malic acid, Biotechnol. Bioeng. 72 (2001) 77–84.

[125] E. Enaud, S. Fleith, F. Naveau, P. Gerin, S. Vanhulle, P. Rouxhet, Coriolopsis polyzona laccase immobilisation by adsorption on a silane-modified porous siliceous carrier and use of the catalytic material for dye synthesis, J. Biotechnol. 150 (Supplement) (2010) S377.

[126] G. Ren, H. Yu, Oriented adsorptive immobilization of esterase BioH based on protein structure analysis, Biochem. Eng. J. 53 (2011) 286–291.

[127] D. Sen, A. Sarkar, A. Gosling, S.L. Gras, G.W. Stevens, S.E. Kentish, P.K. Bhattacharya, A.R. Barber, C. Bhattacharjee, Feasibility study of enzyme immobilization on polymeric membrane: a case study with enzymatically galacto-oligosaccharides production from lactose, J. Membr. Sci. 378 (2011) 471–478.

[128] J.L. Kaar, H.-I. Oh, A.J. Russell, W.J. Federspiel, Towards improved artificial lungs through biocatalysis, Biomaterials 28 (2007) 3131–3139.

[129] D.T. Arazawa, H.-I. Oh, S.-H. Ye, C.A. Johnson Jr, J.R. Woolley, W.R. Wagner, W.J. Federspiel, Immobilized carbonic anhydrase on hollow fiber membranes accelerates CO$_2$ removal from blood, J. Membr. Sci. 403–404 (2012) 25–31.

[130] Y.-T. Zhang, T.-T. Zhi, L. Zhang, H. Huang, H.-L. Chen, Immobilization of carbonic anhydrase by embedding and covalent coupling into nanocomposite hydrogel containing hydrotalcite, Polymer 50 (2009) 5693–5700.

[131] R. Mazzei, L. Giorno, E. Piacentini, S. Mazzuca, E. Drioli, Kinetic study of a biocatalytic membrane reactor containing immobilized β-glucosidase for the hydrolysis of oleuropein, J. Membr. Sci. 339 (2009) 215–223.

[132] A. Sassolas, L.J. Blum, B.D. Leca-Bouvier, Immobilization strategies to develop enzymatic biosensors, Biotechnol. Adv. 30 (2012) 489–511.

[133] Y.-T. Zhang, L.-H. Fan, T.-T. Zhi, L. Zhang, H. Huang, H.-L. Chen, Synthesis and characterization of poly(acrylic acid-co-acrylamide)/hydrotalcite nanocomposite hydrogels for carbonic anhydrase immobilization, J. Polym. Sci. Part A: Polym. Chem. 47 (2009) 3232–3240.

[134] J. Hou, G. Dong, Y. Ye, V. Chen, Laccase immobilization on titania nanoparticles and titania-functionalized membranes, J. Membr. Sci. 452 (2014) 229–240.

[135] J. Hou, G. Dong, Y. Ye, V. Chen, Enzymatic degradation of bisphenol – a with immobilized laccase on TiO$_2$ sol–gel coated PVDF membrane, J. Membr. Sci. 469 (2014) 19–30.

[136] J. Hou, G. Ji, G. Dong, B. Xiao, Y. Ye, V. Chen, Biocatalytic Janus membranes for CO$_2$ removal utilizing carbonic anhydrase, J. Mater. Chem. A 3 (2015) 17032–17041.

[137] M.C. Trachtenberg, C.K. Tu, R.A. Landers, R.C. Willson, M.L. McGregor, P.J. Laipis, J.F. Kennedy, M. Paterson, D.N. Silverman, D. Thomas, R.L. Smith, F.B. Rudolph, Carbon dioxide transport by proteic and facilitated transport membranes, Life Support Biosph. Sci. 6 (1999) 293–302.

[138] I.G. Kim, B.H. Jo, D.G. Kang, C.S. Kim, Y.S. Choi, H.J. Cha, Biomineralization-based conversion of carbon dioxide to calcium carbonate using recombinant carbonic anhydrase, Chemosphere 87 (2012) 1091–1096.

[139] N.J.M.C. Penders-van Elk, E.S. Hamborg, P.J.G. Huttenhuis, S. Fradette, J.A. Carley, G.F. Versteeg, Kinetics of absorption of carbon dioxide in aqueous amine and carbonate solutions with carbonic anhydrase, Int. J. Greenh. Gas Control 12 (2013) 259–268.

[140] S. Zhang, Z. Zhang, Y. Lu, M. Rostam-Abadi, A. Jones, Activity and stability of immobilized carbonic anhydrase for promoting CO$_2$ absorption into a carbonate solution for post-combustion CO$_2$ capture, Bioresour. Technol. 102 (2011) 10194–10201.

[141] L. Xu, L. Zhang, H. Chen, Study on CO$_2$ removal in air by hydrogel membranes, Desalination 148 (2002) 309–313.

[142] M. Saeed, L. Deng, Post-combustion CO$_2$ membrane absorption promoted by mimic enzyme, J. Membr. Sci. 499 (2016) 36–46.

[143] J.A. Franco, D.D. deMontigny, S.E. Kentish, J.M. Perera, G.W. Stevens, Polytetrafluoroethylene (PTFE)-sputtered polypropylene membranes for carbon dioxide separation in membrane gas absorption: hollow fiber configuration, Ind. Eng. Chem. Res. 51 (2011) 1376–1382.

[144] J.A. Franco, S.E. Kentish, J.M. Perera, G.W. Stevens, Poly(tetrafluoroethylene) sputtered polypropylene membranes for carbon dioxide separation in membrane gas absorption, Ind. Eng. Chem. Res. 50 (2011) 4011–4020.

[145] Y. Lv, X. Yu, J. Jia, S.-T. Tu, J. Yan, E. Dahlquist, Fabrication and characterization of superhydrophobic polypropylene hollow fiber membranes for carbon dioxide absorption, Appl. Energy 90 (2012) 167–174.

[146] J.A. Franco, S.E. Kentish, J.M. Perera, G.W. Stevens, Fabrication of a super-hydrophobic polypropylene membrane by deposition of a porous crystalline polypropylene coating, J. Membr. Sci. 318 (2008) 107–113.

[147] Y.-F. Lin, C.-C. Ko, C.-H. Chen, K.-L. Tung, K.-S. Chang, T.-W. Chung, Sol–gel preparation of polymethylsilsesquioxane aerogel membranes for CO$_2$ absorption fluxes in membrane contactors, Appl. Energy 129 (2014) 25–31.

[148] E. Lasseuguette, J.-C. Rouch, J.-C. Remigy, Formation of continuous dense polymer layer at the surface of hollow fiber using a photografting process, J. Appl. Polym. Sci. 132 (2015).

[149] X. Yu, L. An, J. Yang, S.-T. Tu, J. Yan, CO$_2$ capture using a superhydrophobic ceramic membrane contactor, J. Membr. Sci. 496 (2015) 1–12.

[150] V.Y. Dindore, D.W.F. Brilman, F.H. Geuzebroek, G.F. Versteeg, Membrane–solvent selection for CO$_2$ removal using membrane gas–liquid contactors, Sep. Purif. Technol. 40 (2004) 133–145.

[151] G.F. Versteeg, L.A.J. Van Dijck, W.P.M. Van Swaaij, On the kinetics between CO$_2$ and alkanolamines both in aqueous and non-aqueous solutions: an overview, Chem. Eng. Commun. 144 (1996) 133–158.

[152] E. Favre, H.F. Svendsen, Membrane contactors for intensified post-combustion carbon dioxide capture by gas–liquid absorption processes, J. Membr. Sci. 407–408 (2012) 1–7.

[153] E. Chabanon, R. Bounaceur, C. Castel, S. Rode, D. Roizard, E. Favre, Pushing the limits of intensified CO$_2$ post-combustion capture by gas–liquid absorption through a membrane contactor, Chem. Eng. Process.: Process Intensif. 91 (2015) 7–22.

[154] M.W. Arshad, H.F. Svendsen, P.L. Fosbøl, N. von Solms, K. Thomsen, Equilibrium total pressure and CO$_2$ solubility in binary and ternary aqueous solutions of 2-(diethylamino)ethanol (DEEA) and 3-(methylamino)propylamine (MAPA), J. Chem. Eng. Data 59 (2014) 764–774.

[155] Ø. Jonassen, I. Kim, H.F. Svendsen, Heat of absorption of carbon dioxide (CO$_2$) into aqueous N-methyldiethanolamine (MDEA) and N,N-dimethylmonoethanolamine (DMMEA), Energy Procedia 63 (2014) 1890–1902.

[156] L. Ansaloni, L. Deng, Compatible Membrane Materials for 3rd Generation Solvent Membrane Contactors, ICMAT, Singapore, 2015.

[157] H. Bai, A.C. Yeh, Removal of CO$_2$ greenhouse gas by ammonia scrubbing, Ind. Eng. Chem. Res. 36 (1997) 2490–2493.

[158] A.C. Yeh, H. Bai, Comparison of ammonia and monoethanolamine solvents to reduce CO$_2$ greenhouse gas emissions, Sci. Total Environ. 228 (1999) 121–133.

[159] X. Wu, Y. Yu, Z. Qin, Z. Zhang, The advances of post-combustion CO$_2$ capture with chemical solvents: review and guidelines, Energy Procedia 63 (2014) 1339–1346.

[160] C. Makhloufi, E. Lasseuguette, J.C. Remigy, B. Belaissaoui, D. Roizard, E. Favre, Ammonia based CO$_2$ capture process using hollow fiber membrane contactors, J. Membr. Sci. 455 (2014) 236–246.

[161] R.V. Williamson, J.H. Mathews, Rate of absorption and equilibrium of carbon dioxide in alkaline solutions, Ind. Eng. Chem. 16 (1924) 1157–1161.

[162] P.C. Tseng, W.S. Ho, D.W. Savage, Carbon dioxide absorption into promoted carbonate solutions, AIChE J. 34 (1988) 922–931.

[163] S. Yan, Q. He, S. Zhao, Y. Wang, P. Ai, Biogas upgrading by CO$_2$ removal with a highly selective natural amino acid salt in gas–liquid membrane contactor, Chem. Eng. Process.: Process Intensif. 85 (2014) 125–135.

[164] J.G. Lu, A.C. Hua, L.L. Bao, S.X. Liu, H. Zhang, Z.W. Xu, Performance evaluation on complex absorbents for CO$_2$ capture, Sep. Purif. Technol. 82 (2011) 87–92.

[165] J.G. Lu, H. Zhang, Y. Ji, F. Fan, C. Liu, Amino acid-salt-based complex absorbents for CO$_2$ capture in a membrane contactor, Energy Fuel 24 (2010) 4617–4626.

[166] P. Luis, A. Garea, A. Irabien, Zero solvent emission process for sulfur dioxide recovery using a membrane contactor and ionic liquids, J. Membr. Sci. 330 (2009) 80–89.

[167] J. Albo, P. Luis, A. Irabien, Carbon dioxide capture from flue gases using a cross-flow membrane contactor and the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate, Ind. Eng. Chem. Res. 49 (2010) 11045–11051.

[168] L. Deng, Closed Cycle Continuous Membrane Ionic Liquids Absorption/Desorption Process for CO$_2$ Capture, U.K.P. Application (Ed.), 2015.

[169] X. Jie, J. Chau, G. Obuskovic, K.K. Sirkar, Preliminary studies of CO$_2$ removal from precombustion syngas through pressure swing membrane absorption process with ionic liquid as absorbent, Ind. Eng. Chem. Res. 52 (2013) 8783–8799.

[170] J. Chau, G. Obuskovic, X.M. Jie, K.K. Sirkar, Pressure swing membrane absorption process for shifted syngas separation: modeling vs. experiments for pure ionic liquid, J. Membr. Sci. 453 (2014) 61–70.

[171] X. Jie, J. Chau, G. Obuskovic, K.K. Sirkar, Enhanced pressure swing membrane absorption process for CO$_2$ removal from shifted syngas with dendrimer-ionic liquid mixtures as absorbent, Ind. Eng. Chem. Res. 53 (2014) 3305–3320.

[172] Z. Dai, R.D. Noble, D.L. Gin, X. Zhang, L. Deng, Combination of ionic liquids with membrane technology: a new approach for CO$_2$ separation, J. Membr. Sci. 497 (2016) 1–20.

[173] D. Im, K. Roh, J. Kim, Y. Eom, J.H. Lee, Economic assessment and optimization of the Selexol process with novel additives, Int. J. Greenh. Gas Control 42 (2015) 109–116.

[174] E. Chabanon, B. Belaissaoui, E. Favre, Gas–liquid separation processes based on physical solvents: opportunities for membranes, J. Membr. Sci. 459 (2014) 52–61.

[175] F. Bougie, I. Iliuta, M.C. Iliuta, Flat sheet membrane contactor (FSMC) for CO$_2$ separation using aqueous amine solutions, Chem. Eng. Sci. 123 (2015) 255–264.

[176] A.L. Ahmad, A.R. Sunarti, K.T. Lee, W.J.N. Fernando, CO$_2$ removal using membrane gas absorption, Int. J. Greenh. Gas Control 4 (2010) 495–498.

[177] S.-H. Lin, K.-L. Tung, H.-W. Chang, K.-R. Lee, Influence of fluorocarbon flat-membrane hydrophobicity on carbon dioxide recovery, Chemosphere 75 (2009) 1410–1416.

[178] M. Mulder, Basic Principles of Membrane Technology, 2nd ed., Kluwer Academic Publishers Inc., Netherland, 2003.

[179] M.-C. Yang, E.L. Cussler, Designing hollow-fiber contactors, AIChE J. 32 (1986) 1910–1916.

[180] S.R. Wickramasinghe, M.J. Semmens, E.L. Cussler, Mass-transfer in various hollow fiber geometries, J. Membr. Sci. 69 (1992) 235–250.

[181] D. Bhaumik, S. Majumdar, K.K. Sirkar, Absorption of CO$_2$ in a transverse flow hollow fiber membrane module having a few wraps of the fiber mat, J. Membr. Sci. 138 (1998) 77–82.

[182] L. Liu, L. Li, Z. Ding, R. Ma, Z. Yang, Mass transfer enhancement in coiled hollow fiber membrane modules, J. Membr. Sci. 264 (2005) 113–121.

[183] Liqui-Cel, ⟨http://www.liquicel.com/product-information/micromodule.cfm⟩.

[184] K.L. Wang, E.L. Cussler, Baffled membrane modules made with hollow-fiber fabric, J. Membr. Sci. 85 (1993) 265–278.

[185] V.Y. Dindore, G.F. Versteeg, Gas–liquid mass transfer in a cross-flow hollow fiber module: analytical model and experimental validation, Int. J. Heat Mass Transf. 48 (2005) 3352–3362.

[186] S.R. Wickramasinghe, M.J. Semmens, E.L. Cussler, Mass transfer in various hollow

fiber geometries, J. Membr. Sci. 69 (1992) 235–250.

[187] kA. Hoff, Modeling and Experimental Study of CO$_2$ Absorption in a Membrane Contactor, Chemical Engineering Department, Norwegian Univerisity and Science and technology, Trondheim, 2003.

[188] Z. Qi, E.L. Cussler, Hollow fiber gas membranes, AIChE J. 31 (1985) 1548–1553.

[189] P. Luis, T. Van Gerven, B. Van der Bruggen, Recent developments in membrane-based technologies for CO$_2$ capture, Prog. Energy Combust. Sci. 38 (2012) 419–448.

[190] G. Astarita, D.W. Savage, A. Bisio, Gas Treating With Chemical Solvents, John Wiley, United States, 1983.

[191] M.R.M. Abu-Zahra, L.H.J. Schneiders, J.P.M. Niederer, P.H.M. Feron, G.F. Versteeg, CO$_2$ capture from power plants: Part I. A parametric study of the technical performance based on monoethanolamine, Int. J. Greenh. Gas Control 1 (2007) 37–46.

[192] F.A. Tobiesen, H.F. Svendsen, O. Juliussen, Experimental validation of a rigorous absorber model for CO2 postcombustion capture, AIChE J. 53 (2007) 846–865.

[193] R. Dugas, P. Alix, E. Lemaire, P. Broutin, G. Rochelle, Absorber model for CO$_2$ capture by monoethanolamine - application to CASTOR pilot results, Energy Procedia 1 (2009) 103–107.

[194] P. Moser, S. Schmidt, S. Wallus, T. Ginsberg, G. Sieder, I. Clausen, J.G. Palacios, T. Stoffregen, D. Mihailowitsch, Enhancement and long-term testing of optimised post-combustion capture technology - results of the second phase of the testing programme at the niederaussem pilot plant, Energy Procedia 37 (2013) 2377–2388.

[195] T. Neveux, Y. Le Moullec, J.-P. Corriou, E. Favre, Modeling CO$_2$ capture in amine solvents: prediction of performance and insights on limiting phenomena, Ind. Eng. Chem. Res. 52 (2013) 4266–4279.

[196] M.H. Al-Marzouqi, M.H. El-Naas, S.A.M. Marzouk, M.A. Al-Zarooni, N. Abdullatif, R. Faiz, Modeling of CO$_2$ absorption in membrane contactors, Sep. Purif. Technol. 59 (2008) 286–293.

[197] A. Bottino, G. Capannelli, A. Comite, R. Di Felice, R. Firpo, CO$_2$ removal from a gas stream by membrane contactor, Sep. Purif. Technol. 59 (2008) 85–90.

[198] S. Rode, P.T. Nguyen, D. Roizard, R. Bounaceur, C. Castel, E. Favre, Evaluating the intensification potential of membrane contactors for gas absorption in a chemical solvent: a generic one-dimensional methodology and its application to CO$_2$ absorption in monoethanolamine, J. Membr. Sci. 389 (2012) 1–16.

[199] S. Khairsi, D. deMontigny, P. Tontiwachwuthikul, R. Jiraratananon, A mathematical model for gas absorption membrane contactors that studies the effect of partially wetted membranes, J. Membr. Sci. 347 (2010) 228–239.

[200] M. Al-Marzouqi, M. El-Naas, S. Marzouk, N. Abdullatif, Modeling of chemical absorption of CO$_2$ in membrane contactors, Sep. Purif. Technol. 62 (2008) 499–506.

[201] R. Faiz, M. Al-Marzouqi, Mathematical modeling for the simultaneous absorption of CO$_2$ and H$_2$S using MEA in hollow fiber membrane contactors, J. Membr. Sci. 342 (2009) 269–278.

[202] J. Happel, Viscous flow relative to arrays of cylinders, AIChE J. 5 (1959) 4.

[203] N. Boucif, D. Roizard, J.-P. Corriou, E. Favre, To what extent does temperature affect absorption in gas–liquid hollow fiber membrane contactors? Sep. Sci. Technol. 50 (2015) 1331–1343.

[204] E. Chabanon, E. Kimball, E. Favre, O. Lorain, E. Goetheer, D. Ferre, A. Gomez, P. Broutin, Hollow fiber membrane contactors for post-combustion CO$_2$ capture: a scale-up study from laboratory to pilot plant, Oil Gas Sci. Technol. – Rev. IFP Energies Nouv. 69 (2014) 1035–1045.

[205] K.A. Hoff, H.F. Svendsen, Membrane contactors for CO$_2$ absorption - application, modeling and mass transfer effects, Chem. Eng. Sci. 116 (2014) 331–341.

[206] V. Soni, J. Abildskov, G. Jonsson, R. Gani, A general model for membrane-based separation processes, Comput. Chem. Eng. 33 (2009) 644–659.

[207] K.A. Hoff, J. Poplsteinova, H.A. Jakobsen, O. Falk-Pedersen, O. Juliussen, H.F. Svendsen, Modeling of membrane reactor, Int. J. Chem. React. Eng. 1 (2003) 14.

[208] L.U. Kreul, A. Górak, P.I. Barton, Modeling of homogeneous reactive separation processes in packed columns, Chem. Eng. Sci. 54 (1999) 19–34.

[209] P. Kosaraju, A.S. Kovvali, A. Korikov, K.K. Sirkar, Hollow fiber membrane contactor based CO$_2$ absorption-stripping using novel solvents and membranes, Ind. Eng. Chem. Res. 44 (2005) 1250–1258.

[210] S. Koonaphapdeelert, Z. Wu, K. Li, Carbon dioxide stripping in ceramic hollow fibre membrane contactors, Chem. Eng. Sci. 64 (2009) 1–8.

[211] S. Koonaphapdeelert, K. Li, Preparation and characterization of hydrophobic ceramic hollow fibre membrane, J. Membr. Sci. 291 (2007) 70–76.

[212] M. Fang, Z. Wang, S. Yan, Q. Cen, Z. Luo, CO$_2$ desorption from rich alkanolamine solution by using membrane vacuum regeneration technology, Int. J. Greenh. Gas Control 9 (2012) 507–521.

[213] T. Mulukutla, G. Obuskovic, K.K. Sirkar, Novel scrubbing system for post-combustion CO$_2$ capture and recovery: experimental studies, J. Membr. Sci. 471 (2014) 16–26.

[214] Z. Wang, M. Fang, H. Yu, Q. Ma, Z. Luo, Modeling of CO$_2$ Stripping in a Hollow Fiber

Membrane Contactor for CO$_2$ Capture, Energy Fuels 27 (2013) 6887–6898.

[215] M. Fang, S. Yan, Z. Luo, M. Ni, K. Cen, CO$_2$ chemical absorption by using membrane vacuum regeneration technology, Energy Procedia 1 (2009) 815–822.

[216] S. Yan, M. Fang, Z. Wang, Z. Luo, Regeneration performance of CO$_2$-rich solvents by using membrane vacuum regeneration technology: relationships between absorbent structure and regeneration efficiency, Appl. Energy 98 (2012) 357–367.

[217] S. Khairsi, D. deMontigny, P. Tontiwachwuthikul, R. Jiraratananon, CO$_2$ stripping from monoethanolamine using a membrane contactor, J. Membr. Sci. 376 (2011) 110–118.

[218] M. Simioni, S.E. Kentish, G.W. Stevens, Membrane stripping: desorption of carbon dioxide from alkali solvents, J. Membr. Sci. 378 (2011) 18–27.

[219] A. Mansourizadeh, A.F. Ismail, CO$_2$ stripping from water through porous PVDF hollow fiber membrane contactor, Desalination 273 (2011) 386–390.

[220] R. Naim, A.F. Ismail, A. Mansourizadeh, Preparation of microporous PVDF hollow fiber membrane contactors for CO$_2$ stripping from diethanolamine solution, J. Membr. Sci. 392–393 (2012) 29–37.

[221] A. Mansourizadeh, A.F. Ismail, Influence of membrane morphology on characteristics of porous hydrophobic PVDF hollow fiber contactors for CO$_2$ stripping from water, Desalination 287 (2012) 220–227.

[222] M. Rahbari-Sisakht, D. Rana, T. Matsuura, D. Emadzadeh, M. Padaki, A.F. Ismail, Study on CO$_2$ stripping from water through novel surface modified PVDF hollow fiber membrane contactor, Chem. Eng. J. 246 (2014) 306–310.

[223] R. Naim, A.F. Ismail, N.B. Cheer, M.S. Abdullah, Polyvinylidene fluoride and polyetherimide hollow fiber membranes for CO$_2$ stripping in membrane contactor, Chem. Eng. Res. Des. 92 (2014) 1391–1398.

[224] M. Rahbari-Sisakht, A.F. Ismail, D. Rana, T. Matsuura, D. Emadzadeh, Carbon dioxide stripping from water through porous polysulfone hollow fiber membrane contactor, Sep. Purif. Technol. 108 (2013) 119–123.

[225] M. Rahbari-Sisakht, F. Korminouri, D. Emadzadeh, T. Matsuura, A.F. Ismail, Effect of air-gap length on carbon dioxide stripping performance of a surface modified polysulfone hollow fiber membrane contactor, RSC Adv. 4 (2014) 59519–59527.

[226] A. Trusov, S. Legkov, L.J.P. van den Broeke, E. Goetheer, V. Khotimsky, A. Volkov, Gas/liquid membrane contactors based on disubstituted polyacetylene for CO$_2$ absorption liquid regeneration at high pressure and temperature, J. Membr. Sci. 383 (2011) 241–249.

[227] G.A. Dibrov, V.V. Volkov, V.P. Vasilevsky, A.A. Shutova, S.D. Bazhenov, V.S. Khotimsky, A. van de Runstraat, E.L.V. Goetheer, A.V. Volkov, Robust high-permeance PTMSP composite membranes for CO$_2$ membrane gas desorption at elevated temperatures and pressures, J. Membr. Sci. 470 (2014) 439–450.

[228] A.A. Shutova, A.N. Trusov, M.V. Bermeshev, S.A. Legkov, M.L. Gringolts, E.S. Finkelstein, G.N. Bondarenko, A.V. Volkov, Regeneration of alkanolamine solutions in membrane contactor based on novel polynorbornene, Oil Gas Sci. Technol. - Rev. IFP Energies Nouv. 69 (2014) 1059–1068.

[229] C. Sanchez, B. Julian, P. Belleville, M. Popall, Applications of hybrid organic–inorganic nanocomposites, J. Mater. Chem. 15 (2005) 3559–3592.

[230] T.-S. Chung, L.Y. Jiang, Y. Li, S. Kulprathipanja, Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, Prog. Polym. Sci. 32 (2007) 483–507.

[231] P.H.M. Feron, S. Zhao, Membrane Assisted Liquid Absorbent Regeneration (MALAR): Innovative Use of Membranes in Liquid Absorbent Based CO$_2$ Capture, 2013 AIChE Annual Meeting, AIChE, San Francisco, California, 2013.

[232] S. Yan, S. Zhao, L. Wardhaugh, P.H.M. Feron, Innovative use of membrane contactor as condenser for heat recovery in carbon capture, Environ. Sci. Technol. 49 (2015) 2532–2540.

[233] P. Wattanaphan, T. Sema, R. Idem, Z. Liang, P. Tontiwachwuthikul, Effects of flue gas composition on carbon steel (1020) corrosion in MEA-based CO$_2$ capture process, Int. J. Greenh. Gas Control 19 (2013) 340–349.

[234] A.E. Schouten, A.K. van der Vegt, Plastics, Spectrum, 1981.

[235] M. Chanda, S.K. Roy (Eds.), Characteristics of polymers, in: Plastics Technology Handbook. Fourth Edition, CRC Press, 2006, pp. 1-128.

[236] D. Albarracin Zaidiza, J. Billaud, B. Belaissaoui, S. Rode, D. Roizard, E. Favre, Modeling of CO$_2$ post-combustion capture using membrane contactors, comparison between one- and two-dimensional approaches, J. Membr. Sci. 455 (2014) 64–74.

[237] D. Albarracin Zaidiza, B. Belaissaoui, S. Rode, T. Neveux, C. Makhloufi, C. Castel, D. Roizard, E. Favre, Adiabatic modelling of CO$_2$ capture by amine solvents using membrane contactors, J. Membr. Sci. 493 (2015) 106–119.

[238] M. Rahbari-Sisakht, A.F. Ismail, D. Rana, T. Matsuura, Carbon dioxide stripping from diethanolamine solution through porous surface modified PVDF hollow fiber membrane contactor, J. Membr. Sci. 427 (2013) 270–275.

[239] E. Chabanon, D. Roizard, E. Favre, Modeling strategies of membrane contactors for post-combustion carbon capture: a critical comparative study, Chem. Eng. Sci. 87 (2013) 393–407.