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Gas-liquid membrane contactors for carbon dioxide separation: A review

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Abstract

Membrane gas-liquid contactors have been developed to reduce the capital cost and energy consumption of conventional CO_2 absorption and stripping columns. As a hybrid technology of membrane separation and amine absorption, these units can improve the gas absorption process by generating 400-1500% greater mass transfer area per unit volume leading to smaller equipment sizes. Regeneration of CO_2 can occur within a membrane contactor below the boiling point of the solvent, leading to lower energy consumption. Over recent years, a vast array of polymeric and ceramic materials have been considered for membrane gas-liquid contactors and an array of solvents have been used including amines, potassium carbonate, ammonia and amino acids. The major technical challenge with membrane contactors is the wetting of the membrane pores with solvent, which reduces the mass transfer coefficient. However, other factors such as the choice of solvent, the placement of the solvent on the shell or lumen side and the operational temperature are also critical to success. This review describes the recent progress in membrane gas-liquid contactor technology for CO_2 separation in terms of the materials, solvents, modules and processes and provides direction on where research can best be directed in the future to enhance the feasibility of the technology's industrial application.

Keywords:

Membrane contactor, membrane gas absorption, CO_2 separation, carbon capture and storage

1. Introduction

Carbon dioxide (CO_2) is a major focus of separations research as it is a major greenhouse gas and an impurity in natural gas. Raw natural gas can contain a considerable amount of CO_2 that must be removed because it can cause corrosion to pipelines and equipment, reduce the heating value of the gas and prevent effective natural gas liquefaction [1]. Traditionally, CO_2 absorption and subsequent desorption into an amine solvent has been used for this purpose, due to its high reactivity and selectivity. Packed columns are widely used for this operation in refineries, petrochemical plants, natural gas processing and chemical processes using standardised and proven designs (Figure 1(a)). More recently, CO_2 emissions generated by fossil fuel combustion from power plants have become a global issue for climate change [2] and in this situation the amine process is also efficient and effective even though the CO_2 is present at low partial pressure.

CO_2 separation using membrane technology was first developed for natural gas purification as an alternative to amine solvents in the 1980s and has since expanded its market share. Gas separation membranes can selectively permeate target gas molecules due to properties such as the kinetic diameter or chemical interactions between the gas and the material [3-5]. Membrane-based separation is efficient because it does not involve a phase change and this leads to low energy consumption, but its performance is maximised only when the input gas stream has a high partial pressure [6]. At the low partial pressures available in the flue gas from power plants, membrane processes that use commercially available membranes are unable to achieve the necessary purity and selectivity for CO_2, illustrating the need for advanced membranes.

A membrane gas-liquid contactor is a hybrid technique that combines membrane separation and solvent absorption. The membrane separates the gas and liquid phases at the interface, providing the mass transfer contact area for CO_2 absorption and desorption [7] (see

Figure 1(b)). Ideally, the membrane in a CO_2 gas-liquid contactor only permeates CO_2 molecules while rejecting transport of solvent or other gas molecules such as nitrogen (N_2) in flue gas or methane (CH_4) in natural gas. Although all feed components transport through the membrane pores, only CO_2 can diffuse into the solvent due to its high CO_2 selectivity. Compared to a conventional packed column amine process, a membrane contactor provides much greater mass transfer area per unit volume (1500-3000 m^2/m^3) compared to a column contactor (100-800 m^2/m^3) [8]. This is advantageous for offshore natural gas sweetening and brownfield carbon capture processes where space can be limited. Further, regeneration below the boiling point of the solvent becomes possible, by applying a sweep gas or reduced pressure within the desorber unit [9]. This lower temperature desorption reduces energy demand by minimising solvent and water vaporisation. For example, Wang et al. show that a 28% energy saving is possible if the regeneration pressure is 20 kPa [10].

CO_2 separation by membrane contactors consists of two parts: absorption is where CO_2 in the feed gas is selectively absorbed into a lean solvent phase; and desorption, also called stripping, is where CO_2 in a rich solvent is released back as a purified stream for sequestration, as described in Figure 1. The process flow diagrams for both column and membrane contactors are essentially identical, with the column contactors replaced by the membrane modules. The solvent and the gas flow on opposite sides of the membranes, which can be hollow fibres or spiral wound flat sheets. The pores in the membrane act as a fixed and independent interface between the gas and the solvent stream. Unlike most membrane operations, such as microfiltration or gas separation, the driving force for mass transfer is a concentration gradient rather than a pressure gradient, with the selectivity derived from the solvent properties.

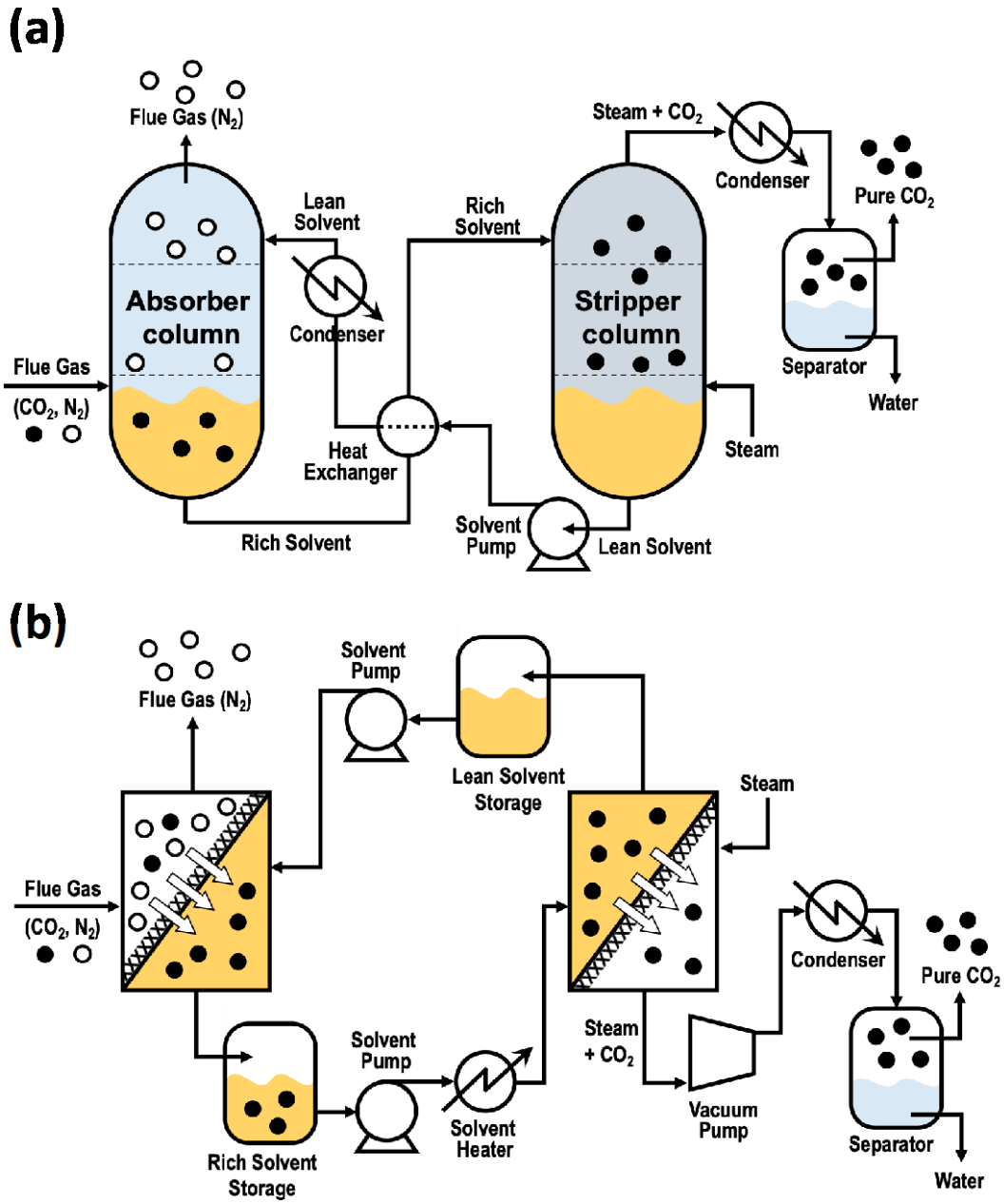

Figure 1. Process flow diagrams of a (a) packed column and (b) membrane contactor for CO_2 capture from flue gas.

Advantages of membrane contactors over columns include operational flexibility, reduced capital costs and an easily predictable design [11]. The modular design allows operation over a wide range of capacities, meaning that scale-up and turndown is straightforward. The membrane configuration facilitates independent manipulation of flow of

both gas and liquid phases. The interfacial area does not vary with operating conditions and this means the overall performance and the loading is more predictable leading to fewer operational issues [12]. A disadvantage is that additional mass transfer resistance arises due to the presence of the membrane. Solvent degradation or gas phase impurities can also cause fouling that can block membrane pores and reduce both mass transfer and the membrane lifetime. Further, the longitudinal pressure drop of both phases can be significantly higher than in a packed column.

Membrane contactors have been commercialised for gas-liquid exchange in a number of other applications [13]. Commercially available modules contain hollow fibre membranes prepared as a homogeneous layer of a non-porous but high free volume rubbery polymer such as poly dimethyl siloxane (PDMS) (e.g. Permselect®); those with a skin layer of such a non-porous polymer on a porous substrate (e.g. Airrane®), those prepared from expanded polytetrafluoroethylene (PTFE) to form a porous membrane (e.g. Markel Eclipse®) and others prepared as an asymmetric fibre with a microporous skin layer by phase inversion of a hydrophobic polymer such as polypropylene (e.g. 3M Liqui-cel®) . These commercial modules are used in applications as diverse as blood oxygenation and carbon dioxide removal (i.e. a heart-lung machine [14]), de-gassing of water, air humidification, provision of chlorine dioxide or ozone as disinfecting agents; and oxygen/CO_2 exchange in wines. Rectangular transverse-flow membrane contactors developed by TNO have been installed in the Netherlands for ammonia recovery, while flat sheet membranes by GVS SpA have been applied for air dehumidification [7].

Membrane distillation is a comparable unit operation where water is evaporated from a liquid phase into a gas stream using a partial pressure gradient driven by differences in temperature and thus vapor pressure. Commercial membrane distillation modules include flat

sheet systems (e.g. Memsys®) and those prepared from flat sheets that are then spiral wound (e.g. AquaStill®).

In this review, we present the latest developments in gas-liquid membrane contactors specifically for CO_2 separation from materials to process design. While there have been a number of reviews on the membrane materials that may be viable in such applications [15-18], the focus in the present case is also on their interaction with emerging solvents. We review applications in CO_2 separation not only from power generation but also from other industrial activities. Specifically, these membrane contactors have been applied in both academia and industry for applications such as natural gas sweetening, biogas purification or syngas cleaning. At the laboratory scale, these studies have focused on the development of new membrane materials that maximise the advantages while solving the current problems of membrane contactors. Additionally, numerous membrane manufacturers have successfully produced membrane modules and processes for industrial, large-scale operations as well as pilot-plant trials.

2. CO_2 absorbent

Liquid absorbents play a critical role in the chemical absorption process in both membrane contactors and column contactors, and numerous solvents have been developed to improve the process efficiency. The selection of the liquid solvents should consider the following criteria; (1) high CO_2 reactivity for absorption capacity and mass transfer, (2) high surface tension for less membrane wetting, (3) moderate viscosity to balance pore wetting versus longitudinal pressure drop, (4) chemical compatibility for long-term stability of membrane materials, (5) low vapor pressure and high thermal stability to reduce solvent loss and (6) ease in regeneration to minimise process energy demand [19]. Among these criteria, CO_2 reactivity and the ease of regeneration have the greatest impact on the capture cost and so

are usually prioritised. The requirements for low vapor pressure and high thermal stability are of greatest importance in reducing the environmental impact of the process and so should also be prioritised for solvent development. Conversely, issues with surface tension and chemical compatibility can be overcome if needed by the development of advanced membrane materials. Amine solvents, most notably monoethanolamine (MEA) are the most widely used for both columns and membrane contactors. Their successful commercialisation has increased the viability of this approach in other industrial applications such as hydrogen sulfide (H_2S) removal. However, amine solvents have a number of drawbacks when used for CO_2 capture, as described in the following section [20-23]. Amino acids, potassium carbonate, aminosilicones, ammonia, ionic liquids or their combinations are examples of alternative solvents.

2.1. Alkanolamines

Alkanolamines are compounds containing both hydroxyl- and amino- functional groups on an alkane backbone. Characteristics of these amine solvents are summarised in Table 1. Primary and secondary amines chemically react with acidic gases such as CO_2 and H_2S in aqueous solution by forming a carbamate. In this case, two amine groups are required for each CO_2 molecule, so the maximum loading is 0.5 mol CO_2/mol amine groups (Table 1). The primary amine, MEA is the most widely used of these solvents [24]. Due to its high alkalinity, it reacts rapidly with CO_2, having the highest CO_2 reaction rate constant. However, the favourable absorption reaction means that CO_2 regeneration is energy intensive. This high regeneration energy means that up to a third of the total output of a power station can be consumed in the carbon capture process [25]. The secondary amines diethanolamine (DEA), diisopropylamine (DIPA) and 2-methylaminoethanol (MAE) have lower absorption reaction rates but lower heat of absorption, leading to lower regeneration energy demands [26-29].

Piperazine (PZ) is a cyclic secondary diamine, which has a high absorption capacity due to the two amine groups and a higher reaction rate than other secondary amines, but again there is a trade-off with a greater heat of absorption leading to greater regeneration energy demand as well as low aqueous solubility. The selection of amine solvent is based on the need to balance the operational costs arising from this high regeneration energy demand against the capital cost associated with the larger equipment sizes needed if reaction rates are low. In post combustion capture from power station flue gases, the regeneration energy demand is usually most critical but there is also a limit to the physical height to which a packed column absorber or stripper can be constructed and this may constrain the solvent choice. In natural gas or biogas sweetening operations, MEA is often used to limit equipment sizes when a high purity gas is required, despite the high regeneration heat [30]. On the other hand, secondary or tertiary amines are used for bulk CO_2 absorption where product purity is less important.

Many of these amines are volatile which leads to solvent loss and can also cause environmental damage. In particular, primary and secondary amines are known to form nitrosamines in the upper atmosphere, which can be carcinogenic [31]. Further, these solvents degrade some membrane materials and adhesives used in membrane contactor designs [20-23]. Degradation of these amines themselves is also a major concern [32], particularly when exposed to free oxygen, SO_x and NO_x which are present in flue gas streams. Aside from the solvent loss, the degraded compounds reduce overall plant efficiency because they can no longer react with CO_2 and because they can lead to increased viscosity, foaming and corrosion [33-35]. Some examples of the degraded products include heat stable salts such as sulfates, formats, acetates and nitrates [35], carboxylic acids, glycine, ammonia, substituted amides, pyridines, substituted alkanols, amines, substituted alkanones, substituted azetidines, substituted aldehydes and polymers [32]. Secondary amines have better oxidation degradation resistance than MEA [26-29].

Tertiary amines such as triethanolamine (TEA) and n-methyldiethanolamine (MDEA) and sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) are unable to form carbamates and hence rely on their intrinsic alkalinity to convert CO_2 to the bicarbonate anion. This means that they have a higher loading capacity (around 1 mol CO_2/mol amine) and less energy is required for regeneration [26-29]. However, the reaction rate for CO_2 absorption for these amines is generally low. The boiling point and vapor pressure of each solvent should also be considered to prevent solvent loss and reduce solvent degradation. 1-dimethylamino-2-propanol (1DMA2P) has been considered as a promising tertiary amine with a relatively high reaction rate and CO_2 capture capacity [36]. This led to a much higher CO_2 flux than MDEA when used in a membrane contactor. Some other examples of tertiary amines are the series of newly synthesised amines, called 1-(2-hydroxyethyl)pyrrolidine (1-(2-HE)PRLD), 4-(dimethylamino)-2-butanol (DMAB), 1-(2-hydroxyethyl)-piperidine (1-(2-HE)PP), 4-((2-hydroxyethyl)(ethyl)amino)-2-butanol (HEEAB), 4-((2-hydroxyethyl)(methyl)amino)-2-butanol (HEMAB), 3-diethylamino-1,2-propanediol (DE-1,2-PD) and 4-(dipropylamino)-2-butanol (DPAB) [37, 38]. In a simulation study, these amines showed high CO_2 absorption capacity and cyclic capacity based on their low heat of CO_2 absorption and high absorption rate. However, further evaluations on mass transfer, corrosion, degradation and other parameters are required for these amines to be used in practical applications. Some amine solvents are not very practical due to their low boiling point, high viscosity and high vapor pressure despite having good CO_2 loading capacity.

Table 1. Characteristics of typical amine solvents.

	Boiling point (°C)	Vapor pressure at 20 °C (Pa)	ΔH at 40 °C (kJ/mol CO_2)	Ref.
Primary amines				
Monoethanolamine (MEA)	170	64	-85.1	[26, 28]
1-amino-2-propanol (1A2P)	159	63	-85.5	
Isobutylamine (IBA)	63	13,500	-97	
Ethylamine	16	116,500	n/a	[27]
Propylamine	47	33,000	n/a	
Butylamine (BA)	77	9,100	n/a	
Primary double amines				
1,3-diaminopropane (DAP)	139	1,533	-97.2	[26, 28]
Hexamethylenediamine (HMD)	204	-	-98.4	
Secondary amines				
Diethanolamine (DEA)	271	<1	-74.2	[26]
Piperazine (PZ)	146	21	-80.6	
2-(tert-butylamino)ethanol (2TBAE)	90	37	-80.6	[26, 28]
2-(methylamino)ethanol (2MEA)	160	930	-73.8	[26, 29]
2-(ethylamino)ethanol (2EAE)	170	<100	-69	
2-(isopropylamino)-ethanol (IPMEA)	182	<133	n/a	
2-(benzylamino)ethanol (BZMEA)	199	0.178	n/a	
2-(butylamino)ethanol (2BAE)	156	67	-74.4	
Diethylamine (DA)	55	24000	-87.2	[26]
Tertiary amines				
Triethanolamine (TEA)	335	1	-66.6	[26, 28]
N-methyldiethanolamine (MDEA)	247	1	-52.5	
2-(dimethylamino)ethanol (DMEA)	134	816	-63.3	
1-dimethylamino-2-propanol (1DMA2P)	121	1066	-60.7	[26]
N,N-diethylethanolamine (DEEA)	161	100	-73.2	
3-dimethylamino-1-propanol (3DMA1P)	163	-	-54.6	
N,N,N',N'-Tetramethyl-1,3-propanediamine (TMPAD)	145	650	-59.9	
3-(dimethylamino)propylamine (3DMAPA)	129	666	-91.3	
Sterically hindered primary amines				
2-amino-1-methyl-2-propanol (AMP)	165	<133	-80.9	[26, 28]
2-amino-1-butanol (2A1B)	178	43	-82.5	
Sec-butylamine (SBA)	77	18,000	-96.7	

Isopropylamine (IPA)	31	63410	-93.2	[26]
N-pentylamine	105	3,920	n/a	[27]

A blend of a primary amine such as MEA with a tertiary amine such as MDEA, can improve the CO_2 absorption capacity from the tertiary amine while maintaining a high reaction rate from the primary amine. As reported by Kim et al. in their theoretical analysis, the combination of MEA and PZ, or MEA and diethylenetriamine increased the CO_2 absorption capacity compared with MEA alone, while an MEA blend with AMP or DEA decreased performance [39]. A blend of 2-(dimethylamino)ethanol (DMEA) and PZ in membrane contactor operations increased CO_2 flux up to 50% more than for pure DMEA [40]. Brúder et al. reported that an aqueous solution of PZ and AMP gave the advantage of a lower regeneration temperature due to the AMP and a fast reaction rate due to the PZ [41]. Van Loo et al. show that these fast reacting amines are consumed first, so only have impact at the solvent entry end of the absorber [42]. However, it is in this region that CO_2 gas phase concentrations are low and hence the promotion of the reaction rate can result in a significant reduction in the overall mass transfer area required.

2.2. Electrolyte Systems

Electrolyte alternatives have been proposed to overcome the issues associated with the volatility and environmental concerns of the alkanolamines. Amino acids are one such class that retain the reaction mechanisms of the alkanolamines but are non-volatile and much less toxic. Examples include glycine, lysine, histidine, taurine, sarcosine and alanine [43-46]. The use of such amino acids for CO_2 capture has been commercialised through the BASF Alkazid™ Process and the Siemens PostCap™ process [44].

Potassium carbonate (K_2CO_3) is a further example of an electrolyte that has been commercially used for CO_2 removal in ammonia and methanol manufacturing, as well as acidic

gas removal from ammonia syngas, crude hydrogen, natural gas [47, 48]. The K_2CO_3 based absorption system, called the Benfield process, is advantageous as the species is non-volatile, has high CO_2 solubility, is cheap, non-toxic and does not degrade. Like tertiary amines, the absorption of CO_2 occurs by base catalysis forming bicarbonate. Solvent regeneration can occur at lower temperatures than MEA and with less energy demand, making the regeneration process more efficient and economical, with the total energy demand only 40% of the amine system [49-51]. However, the use of reaction rate promotors such as PZ, DEA or amino acids are required due to the poor reaction rate with CO_2. The addition of small concentrations of such promotors enhances the CO_2 conversion through a zwitterion intermediate [52]. Precipitation of K_2CO_3 crystals can be an issue in membrane contactors [53], but conversely can be used to reduce regenerating energy in a contactor system [54, 55].

2.3. Ionic liquids

Ionic liquids (ILs) are organic salts that are in the liquid state at ambient temperature, due to the use of bulky and asymmetric organic compounds as the cation and/or anion [56-58]. Numerous ILs can be synthesised by the choice of either anion or cation with specific functionality. These ILs can be promising CO_2 solvents as they have extremely low vapor pressure which prevents solvent release to the environment and high thermal stability that reduces solvent degradation [58]. In addition, a number of ILs are regarded as novel alternatives for amine-based solvents because of their higher CO_2 solubility which reduces the quantity of solvent required [59, 60]. Generally, CO_2 absorption in ILs is by physical dissolution. However, ILs with amine group functionality can form a chemical bond with CO_2, such as those with an imidazolium cation [61]. The superbase ILs prepared from 1,8-diazabicyclo[5,4,0]undec-7-ene [HDBU] with imidazole [Im], indole [Ind] or 1,2,4-triazole [Triz] showed CO_2 absorption capacity up to 0.141 g CO_2/g IL [62]. The imidazolium ILs

synthesised by 1-(3-aminopropyl)-3-(2-aminoethyl)imidazolium [Apaeim], 1-ethyl-3-(2-aminoethyl)imidazolium [Eaeim], and 1-propyl-3-(2-aminoethyl)imidazolium [Paeim] as the cation; with hydroxide [OH], L-alaninate [ala], glycinate [gly], and valinate [val] as the anion demonstrated CO_2 loading up to 4.72 mol CO_2/mol IL with a rapid desorption rate [63]. Such ILs are regarded as novel alternatives for amine-based solvents because of their higher CO_2 solubility which reduces the quantity of solvent required [59, 60].

Ionic liquids can be very hygroscopic in nature, which means they become diluted upon exposure to a wet feed gas such as in post-combustion capture, reducing their net capacity. A further issue with these compounds can be their high viscosity, which can often increase even further after absorbing CO_2 [64]. Venkatraman et al. [65] reported a computational screening strategy that could predict the viscosity of ILs based on machine learning. For example, they showed that the sulphonium ionic liquids are less viscous due to the larger size of the sulphur atom. ILs containing hexafluoroacetylacetonate, acetate or phenolate anions were predicted to have viscosity below 300 mPa.s. However, these ILs lack the amine functional groups that enable chemisorption and thus provide high CO_2 solubility. Dilution with water or amine solvents such as MEA and MDEA can reduce the viscosity, but this sacrifices the advantages of ILs [66]. Supported IL membranes or composite membranes containing immobilised ILs in the membrane phase may offer one alternative to prevent the viscosity increase while retaining CO_2 absorption capacity [67]. Encapsulation of ILs within capsules has also been shown to enhance absorption and desorption kinetics due to the high surface areas of these particles without losing CO_2 absorption capacity [68, 69].

2.4. Other solvents

Short chain length aminosilicones have been tested as non-aqueous solvents for CO_2 absorption. The lack of an aqueous phase and their high boiling points of over 250 ºC, means

that latent heats of evaporation are minimised, reducing the regeneration energy demand [70, 71]. For example, polydimethylsiloxanes (PDMS) functionalised with side chain amine groups present low vapor pressure and high thermal stability with high CO_2 solubility [72]. Structural variation of these aminosilicones has been investigated to potentially improve the CO_2 absorption capability, with both CO_2-philic backbones and CO_2-reactive functional groups for both physisorption and chemisorption [71]. The use of relatively high CO_2 absorption and desorption temperatures is also advantageous for improving process efficiency. Some aminosilicones, such as 1,3-Bis(3-aminopropyl)-1,1,3,3-tetramethyldsiloxane undergo a reversible phase change from liquid to solid as the carbamate salt forms during CO_2 absorption [72-74]. As with the precipitating potassium carbonate system, a significant advantage in this case is that only the solid needs to be processed through the regeneration system. This reduces both the size and energy demand from this regeneration step [72].

Ammonia solutions are similarly capable of CO_2 absorption, forming ammonium carbonate at ambient temperatures [75]. These solutions have fewer environmental effects and lower toxicity than amine solutions, but the strong volatility of ammonia requires the process to be operated below 10 ºC, which means that refrigeration systems are required. Ammonia has a lower heat of CO_2 absorption, which should lead to a lower regeneration energy demand, but in practice this is not observed due to the energy required to heat the cold rich solvent to the regeneration temperature and the latent heat arising from ammonia volatilisation. However, some advanced flash strippers have demonstrated reduced regeneration energy and enhanced CO_2 removal capacity by optimising process parameters, such as pressure and ammonia concentration [76, 77].

In summary, the choice of solvent plays a critical role in CO_2 absorption and stripping as it can strongly influence the energy use and the mass transfer area. Although the majority of the work to date has focused on MEA as a solvent due to its proven performance, alkanolamines

are corrosive and readily degraded, leading to a loss of solvent efficiency. Intensive studies on alternatives such as amino acids or other electrolytes are required. However, more importantly, their extensive characterisation and pilot plant demonstration is needed to facilitate full commercialisation.

3. Membrane materials

The development of membrane materials is fundamental for membrane contactor applications. These materials need to be an effective barrier between the gas and liquid phases; however, they do not need to be selective for CO_2, making the material selection easier than for gas separation membranes. The material must be thermally and chemically compatible with the solvent and operating conditions and it must be processable to ensure it can be manufactured at scale for moderate cost.

Ideally, the membrane is sufficiently porous so that it does not hinder natural CO_2 diffusion into the solvent but is still able to prevent the solvent from entering the pores. Such pore wetting significantly reduces the CO_2 mass transfer rate, as the mass transfer coefficient through liquid filled pores is orders of magnitude lower than that if the pores are gas filled (see Figure 2). The susceptibility of a membrane/solvent system to pore wetting can be characterised by the Young-Laplace equation (Equation (1)) which describes the breakthrough pressure (p_B) at which the solvent will freely flow through the material [78]:

$$p_B = \frac{4\gamma cos\theta}{d_{max}} \quad (1)$$

where γ is the surface tension of the solvent, θ is the contact angle of the material, which is indicative of its interaction with the solvent and d_{max} is the maximum pore diameter.

In practice, pore wetting occurs at pressure differentials below this value, but the equation provides a guide as to the important control parameters. That is, a membrane material with a high contact angle with the solvent will be resistant to pore wetting. As most solvents

are aqueous, a high contact angle implies a hydrophobic material is preferable. Polymers such as polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polysulfone (PSf), and polyetherimide (PEI) have been widely studied and applied to industrial operations for this reason. However, solvents such as MDEA have a lower surface tension and contact angle with the membrane than pure water [79], which increases the potential for pore wetting. Similarly, both the amine solvents and their degradation products such as formic, acetic or oxalic acid can absorb into the membrane material over time, altering the surface properties and reducing the contact angle [21].

A membrane with small pores will resist wetting, but there is a trade-off as smaller pores will also reduce the rate of CO_2 mass transfer [80]. The pore size is usually within a range such that gas transport through this layer is a combination of Poiseuille and Knudsen flow [81]. As Equation 1 above involves the maximum pore diameter, it is also important to ensure a narrow pore size distribution, with no membrane defects. Both the surface tension of the liquid and the contact angle fall as temperature increases and thus membranes are generally more easily wetted at higher temperature [79].

Another approach to reduce the membrane wetting is by coating an ultrathin and non-porous layer onto the porous membrane surface. The solvent cannot penetrate this layer while CO_2 molecules can permeate via the solution-diffusion mechanism. This results in pores that remain gas filled. However, the coating layer provides additional resistance for CO_2 transport that can significantly decrease flux. Such thin film composite membranes are known to be advantageous for long-term operation as CO_2 membrane contactors since the initial performance is generally maintained [82]. However, if the dense skin layer is hydrophilic and the underlying porous sub-structure pore size is small, water can permeate as a vapor and condense within the pores, leading to a decline in performance with time [82, 83].

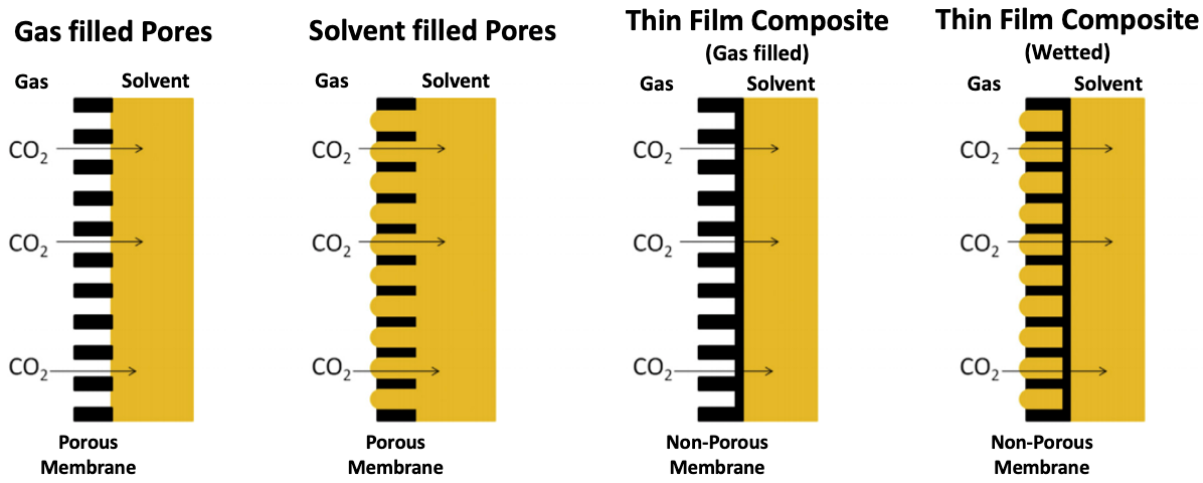

Figure 2. Schematic of CO_2 absorption through a gas filled porous membrane contactor and a thin film composite membrane contactor with both dry and wetted porous support. Reprinted with permission from [82]. Copyright 2015 Elsevier.

3.1. Polymeric membranes

Polymers have been the most popular membrane materials for membrane contactors because of their good performance, low cost, and ease of membrane fabrication [85, 86]. Phase inversion is the most widely used method for the membrane fabrication. This includes non-solvent induced phase separation (NIPS) where the polymer precipitates from a solution when a non-solvent is introduced; and thermally induced phase separation (TIPS); where the polymer precipitates when its melt is cooled down [86-88]. Hollow fibre membranes are usually formed from a NIPS process, where the polymer is dissolved into a solvent forming a viscous dope, which is then extruded through a spinneret. The newly formed hollow fibre passes through an air gap and then into a non-solvent bath, usually water. Membranes produced by this phase inversion process have an asymmetric pore structure, which is controlled by the time between fibre formation and immersion within the non-solvent. The characteristics of the resulting membranes depends on the polymer properties, the choice of solvents and non-solvent, fabrication conditions and the use of additives such as surfactants. In particular, the selection

of a suitable solvent, considering its affinity with the polymer and non-solvent, is important. As described in Figure 3, the structure of the asymmetric membranes can be classified into either a sponge-like structure or a structure with finger-like macrovoids. A rapid diffusion of the non-solvent into the membrane causes these large finger-like macrovoids [88]. Their high porosity facilitates rapid mass transport but provides low mechanical strength. A range of polymers including PVDF, PSf, PP and PEI, can be prepared into such asymmetric membranes by phase inversion. Other polymers such as PE or PTFE are prepared by thermal extrusion, followed by a stretching or expansion process to provide the microporous structure. Examples of polymers for membrane contactors are listed in Figure 4 with their chemical structures, while characteristics of typical polymer membranes used in membrane contactors including their preparation conditions such as dope solution composition and bore fluid are given in Table 2, with their performance in absorption in Table 3 and stripping in Table 4.

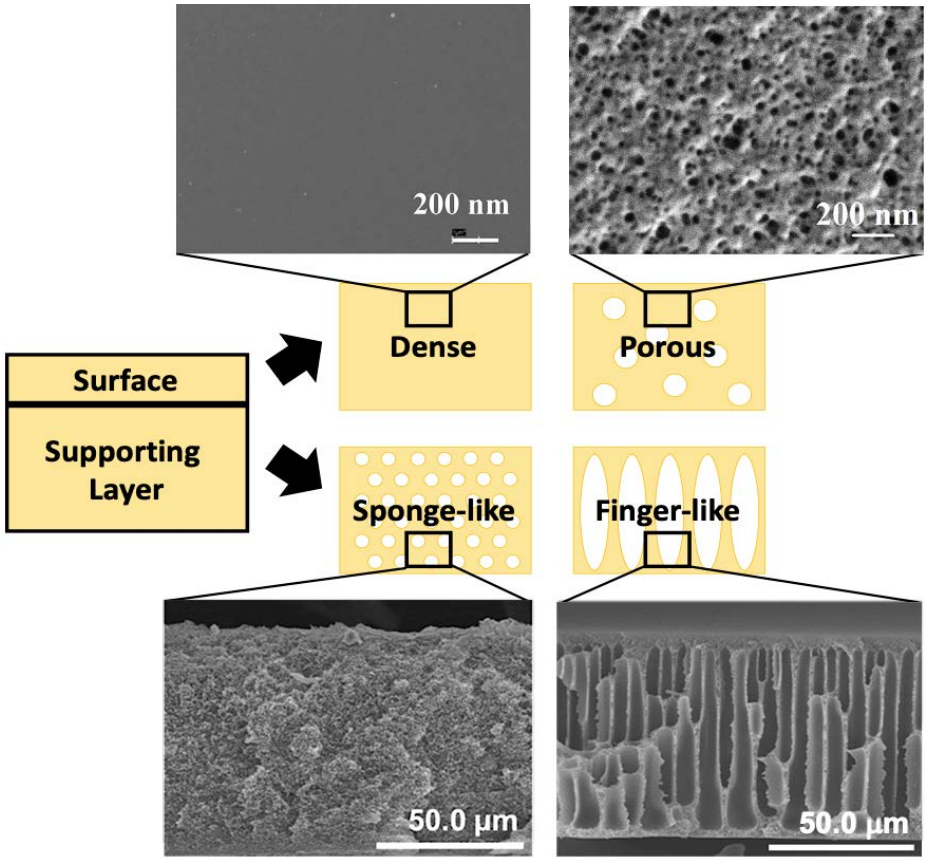

Figure 3. Schematic of membrane morphologies with SEM images. Reprinted with permission from [87, 88]. Copyright 2019 Elsevier.

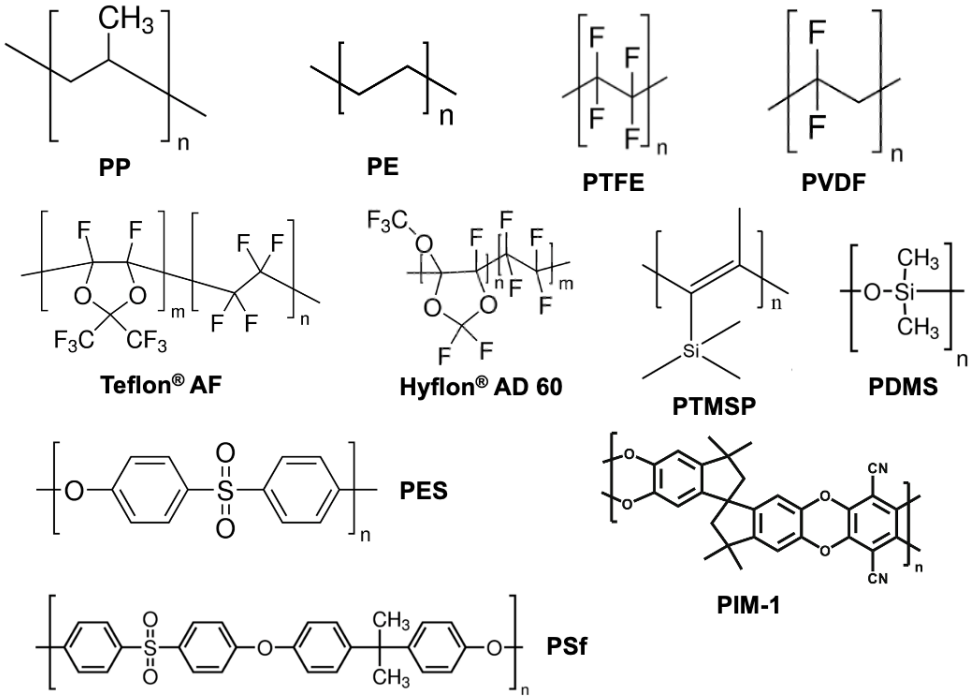

Figure 4. Chemical structures of typical polymers for membrane contactors.

Table 2. Characteristics of porous membrane contactors.

	Dope solution	Bore fluid	Note for membrane preparation	Average pore size (nm)	Effective surface porosity, ε/L_p (m^{-1})	Overall porosity (%)	Breakthrough pressure (10^5 Pa)	Contact angle (°)	Ref.
PEI	PEI 15 wt% in NMP	NMP/Water (80/20 wt%)	-	27	29.7	80	6.5	-	[89]
PEI-Acetone	PEI 15 wt% in NMP/additive (95/5 wt%)		Additive (acetone, EtOH or glycerol) mixed in solvent	12	108	76	7.0	-	
PEI-EtOH				49	65.4	84	6.0	-	
PEI-Glycerol				9.0	60.2	75	8.0	-	
PEI	PEI 17 wt% in NMP	NMP/Water (70/30 wt%)	-	210	125	-	9	75	[90]
PEI-PEG400	PEI 17 wt% in NMP/PEG400 (78/5 wt%)		PEG400 as an additive mixed in solvent	140	136	-	>10	71	
PEI	PEI 18 wt% in NMP	NMP/Water (90/10 wt%)	-	31	38.8	73	7.5	71	[91]
PEI-EtOH 2wt%	PEI 18 wt% in NMP/EtOH		Solvent NMP/EtOH (98/2 wt%)	25	75.1	76	7.5	79	
PEI-EtOH 4wt%			Solvent NMP/EtOH (96/4 wt%)	35	25.4	73	6.5	72	
PEI	PEI 15 wt% in NMP	Water	-	1100	390	79	3.0	77	[92]
PEI-PA	PEI 15 wt% in NMP/additive (81/4 wt%)		Additive (PA, MeOH or LiCl) mixed in solvent	1100	2240	81	5.0	71	
PEI-MeOH				450	3310	81	3.5	77	
PEI-LiCl				3700	50	80	4.0	83	
PSf	PSf 18 wt% in NMP	NMP/Water (90/10 wt%)	-	25	48.6	71	7.5	68	[93]
PSf-EtOH 2 wt%	PSf 18 wt% in NMP/EtOH (80/2 wt%)		EtOH as an additive mixed in solvent	19	76.3	75	8.0	73	
PSf 0% NMP	PSf 18 wt% in NMP/glycerol (96/4 wt%)	Water	-	47	121	62	5.0	-	[94]
PSf 50% NMP		NMP/Water (50/50 wt%)	-	73	37	72	4.5	-	
PSf 70% NMP		NMP/Water (70/30 wt%)	-	140	9	74	4.0	-	
PSf 90% NMP		NMP/Water (90/10 wt%)	-	370	1.5	75	4.0	-	
PTFE	-	-	Commercial flat sheet membranes	200	-	13	0.9	126	[83]
PALL Supor 200R	-	-		200	-	27	1.1	142	

PVDF	PVDF 17 wt% in NMP	NMP/Water (70/30 wt%)	-	350	154	-	5.0	89	[90]
PVDF-PEG400	PVDF 17 wt% in NMP/additive (78/5 wt%)		PEG400 as an additive mixed in solvent	300	175	-	6.5	85	
PVDF-PA	PVDF 18 wt% in NMP/additive (78/4 wt%)	NMP/Water (80/20 wt%)	PA or $LiCl.H_2O$ as an additive mixed in solvent	9.5	54.9	72	6.5	86	[95]
PVDF-$LiCl.H_2O$				5.7	198	65	6.0	87	
PVDF	PVDF 17 wt% in NMP	NMP/Water (70/30 wt%)	-	7.8	259	-	2.5	85	[96]
PVDF-PEG400	PVDF 17 wt% in NMP/additive (78/5 wt%)		Additive (PEG400, EtOH, glycerol or PA) mixed in solvent	5.2	190	-	5.5	85	
PVDF-EtOH				6.5	680	-	1.5	89	
PVDF-Glycerol				9.6	155	-	4.0	84	
PVDF-PA				5.8	321	-	4.0	84	
PVDF	PVDF 18 wt% in NMP	NMP/Water (80/20 wt%)	-	54	95.7	-	5.0	85	[97]
PVDF-PA 2%	PVDF 18 wt% in NMP/PA		Solvent NMP/PA (80/2 or 74/8 wt%)	46	105	-	6.5	83	
PVDF-PA 8%				17	113	-	9.0	79	
PVDF-LiCl 2%	PVDF 18 wt% in NMP/LiCl		Solvent NMP/LiCl (80/2 or 74/8 wt%)	44	105	-	6.0	82	
PVDF-LiCl 8%				29	60.1	-	8.5	78	
PVDF	PVDF 17 wt% in DMAc	DMAc/Water (80/20 wt%)	-	860	3.2	-	3.0	85	[98]
PVDF-LiCl 3%	PVDF 17 wt% in DMAc/LiCl		Solvent DMAc/LiCl (80/3 or 78/5 wt%)	40	1210	-	6.0	80	
PVDF-LiCl 5%				28	2310	-	7.0	75	
PVDF-HFP	PVDF-HFP 18 wt% in NMP	NMP/Water (70/30 wt%)	-	90	174	86	2.0	93	[99]
PVDF-HFP-PEG400	PVDF-HFP 18 wt% in NMP/additive (78/4 wt%)		Additive (PEG400 or PA) mixed in solvent	45	697	85	2.5	93	
PVDF-HFP-PA				15	3980	83	3.5	92	
PVDF	PVDF 20 wt% in NMP with additional 1 wt% ammonia water (25-28%)	Water	-	57	628	78	3.5	87	[80]
PVDF-HDTMS-0.5			Additional 0.5, 1.5 or 5.0 wt% of HDTMS in the dope solution	49	575	78	6.5	132	
PVDF-HDTMS-1.5				39	405	76	7.5	150	
PVDF-HDTMS-5.0				16	130	74	5.0	150	
PVDF	PVDF 18 wt% in NMP/PA (76/6 wt%)	NMP/Water (80/20 wt%)	-	26	107	-	8.5	80	[100]
PVDF-PTFE 1%			Additional 1, 5 or 9 wt% of PTFE in the dope solution	32	117	-	9.0	88	
PVDF-PTFE 5%				40	146	-	10	92	
PVDF-PTFE 9%				57	115	-	8.5	95	
PVDF	PVDF 18 wt% in NMP/LiCl (79.5/2.5 wt%)	NMP/Water (80/20 wt%)	-	130	26	67	6.5	83	[101]
PVDF-MWCNT 3			Additional 3, 5 or 7 wt% of MWCNT in the dope solution	91	136	78	8.5	96	
PVDF-MWCNT 5				78	209	82	10	103	
PVDF-MWCNT 7				220	70	85	5.5	87	

PVDF	PVDF 15 wt% in NMP/PEG400 (80/5 wt%)	-	Flat sheet membrane	410	-	82	1.5	115	[102]
PVDF-Graphene 1			Flat sheet membrane, additional 1, 3 or 7 wt% of graphene in the dope solution	390	-	83	1.7	125	
PVDF-Graphene 3				360	-	85	1.8	125	
PVDF-Graphene 7				350	-	86	1.9	133	
PVDF	PVDF 18 wt% in NMP/LiCl (79.5/2.5 wt%)	NMP/Water (80/20 wt%)	-	26	87	-	8.0	80	[103], [104]
PVDF-MMT 1			Additional MMT in 1, 3 or 5 wt% by polymer in the dope solution	32	124	-	9.5	84	
PVDF-MMT 3				34	171	-	9.0	88	
PVDF-MMT 5				22	237	-	11	99	
PVDF	PVDF 18 wt% in NMP/LiCl (79.5/2.5 wt%)	Water	-	130	19	-	7.5	84	[105]
PVDF-ZSM5 1			Additional 1, 3 or 5 wt% of ZSM5 in the dope solution	69	93	-	10	91	
PVDF-ZSM5 3				48	203	-	12	97	
PVDF-ZSM5 5				59	293	-	11	104	
PVDF-4%SiO_2-30	PVDF 18 wt% in NMP	NMP/Water (30/70 wt%)	Additional 4 or 2 wt% of SiO_2 in the dope solution	37	114	-	10	99	[106]
PVDF-4%SiO_2-50		NMP/Water (50/50 wt%)		44	128	-	9.5	110	
PVDF-4%SiO_2-80		NMP/Water (80/20 wt%)		58	156	-	9.5	147	
PVDF-2%SiO_2-80				42	128	-	9.0	140	
PVDF	PVDF in NMP	-	-	230	-	-	-	141	[107]
PVDF-PBI 15 wt%			Flat sheet membrane, PBI 15, 20 or 25 wt% by PVDF	340	-	-	-	144	
PVDF-PBI 20 wt%				470	-	-	-	142	
PVDF-PBI 25 wt%				350	-	-	-	134	
PVDF	-	-	Commercial PVDF hollow fibre	100	-	-	-	107	[108]
PVDF-TiO_2-2	-	-	TiO_2 coating on PVDF hollow fibre	-	-	-	-	81	
PVDF-fTiO_2-1	-	-	Fluorination after TiO_2 coating	60	-	-	-	119	
PVDF-fTiO_2-2	-	-		25	89	-	-	125	
PVDF-fTiO_2-SiO_2-0.5	-	-	TiO_2 and SiO_2 coating on PVDF hollow fibre, fluorination after coating.	260	-	-	-	117	[109]
PVDF-fTiO_2-SiO_2-1	-	-		25	-	-	-	124	
Al_2O_3 1200°C	PES/Al_2O_3 in NMP/PVP	Water		160	20100	-	-	53	[110]

Al_2O_3 1200°C FAS			Hollow fibre sintered at 1200 or 1500 °C, FAS for fluoroalkylsilane treatment after sintering	140	24500	-	-	125	
Al_2O_3 1500°C				80	8360	-	-	83	
Al_2O_3 1500°C FAS				110	8930	-	-	105	
ZrO_2 on Al_2O_3 FAS	-	-	-	200	-	38	6.5	153	[111]
Al_2O_3 A FAS	PES/Al_2O_3 in NMP/PVP	Water	A, B, C for different extrusion flowrate and pressure, and air gap distance, sintering at 1300 °C	-	-	60	2.6	120	[84]
Al_2O_3 B FAS				-	-	49	-	-	
Al_2O_3 C FAS				-	-	54	-	-	
Al_2O_3	PES/Al_2O_3 in NMP/PVP	Water	Sintering at 1300 °C	157	-	60	1.1	< 90	[112]
Al_2O_3 FAS				-	-	-	3.0	125	
Al_2O_3 FAS	PES/Al_2O_3 in NMP/PVP	Water	Sintering at 1300 °C	68	5660	46	4.8	126	[113]
Al_2O_3 FAS	-	-	Commercial flat sheet membrane	-	-	-	-	140	[114]
Al_2O_3-SiO_2 FAS-1	-	-	FAS treatment, repeated 1, 3 or 5 times after SiO_2 modification	-	-	-	-	141	
Al_2O_3-SiO_2 FAS-3	-	-		-	-	-	-	147	
Al_2O_3-SiO_2 FAS-5	-	-		-	-	-	-	150	
Kaolin-Al_2O_3 FAS	PES/Al_2O_3/Kaolin in NMP/Arlacel P135	Water	Sintering at 1450 °C, FAS treatment	-	-	-	2.5	142	[115]

Table 3. CO_2 absorption properties of membrane contactors.

	Solvent	Solvent Side	Solvent Reynolds number[a]	Gas	Gas Reynolds Number[a]	CO_2 flux (mmol/m^2 s)	Ref.
PEI	DI water	Lumen	1670	Pure CO_2	20	0.80	[89]
PEI-Acetone						0.75	
PEI-EtOH						0.88	
PEI-Glycerol						0.47	
PEI	1M MEA	Lumen	500	Pure CO_2	n/a	18	[92]
PEI-PA						26	
PEI-MeOH						20	
PEI-LiCl						20	
PSf	1M MEA	Shell	150	Pure CO_2	30	2.1	[93]
PSf-EtOH 2 wt%						3.9	
PSf 0% NMP	DI water	Shell	220	Pure CO_2	100	0.14	[94]
PSf 50% NMP						0.25	
PSf 70% NMP						0.27	
PSf 90% NMP						0.29	
PVDF-PA	DI water		1470	CO_2/CH_4 (20/80)	n/a	0.2	[95]
PVDF-LiCl.H_2O				Pure CO_2		0.54	
PTFE						0.39	
PP						0.38	
						0.15	
PTFE	2M DMEA	Lumen	100	CO_2/Air (15/85)	80	1.2	[40]
	2M DMEA + 0.2M PZ					1.8	
	2M DMEA + 0.2M MEA					1.5	
	2M DMEA + 0.2M AMP					1.3	
PTFE	2M MDEA	Lumen	100	CO_2/Air (15/85)	80	0.5	[36]
	2M 1DMA2P					0.9	
PDMS	30 wt% MEA	Shell	n/a	CO_2/N_2 (12.3/77.6)	n/a	2.3	[9]
Porous PEEK	40 wt% aMDEA	Shell	n/a	CO_2/Air (16.6/83.4)	n/a	1.3	[116]
PVDF	DI water	Shell	320	Pure CO_2	10	0.60	[96]
PVDF-PEG400						0.65	
PVDF-EtOH						0.55	
PVDF-PA						0.65	
PVDF- Glycerol						0.79	
		Shell	110			0.56	
				CO_2/N_2 (20/80)		0.34	
PVDF	DI water	Shell	110	CO_2/N_2 (19/81)	2	0.25	[97]
PVDF-LiCl 2%						0.27	

PVDF-LiCl 8%						0.38	
PVDF-PA 2%						0.30	
PVDF-PA 8%						0.41	
			150		20	1.31	
PVDF-HFP	DI water	Shell	150	Pure CO_2	70	1.3	[99]
PVDF-HFP-PEG400						1.7	
PVDF-HFP-PA						2.0	
PVDF-PA-8	1M DEA	Shell	60	CO_2/N_2 (19/81)	2	0.99	[80]
PVDF-HDTMS-0.5						1.8	
PVDF-HDTMS-1.5						2.2	
PVDF-HDTMS-5.0						2.1	
PVDF	DI water	Shell	100	CO_2/N_2 (19/81)	3	0.42	[100]
					10	0.81	
	1M DEA		60			1.7	
PVDF-PTFE 1%						1.8	
PVDF-PTFE 5%						2.0	
PVDF-PTFE 9%						1.8	
PVDF	0.1 wt% Al_2O_3 nanofluid	Lumen	1500	Pure CO_2	S, 150	1.3	[101]
PVDF-MWCNT 3						2.9	
PVDF-MWCNT 5						3.9	
PVDF-MWCNT 7						2.4	
PVDF	DI water	Flat Sheet Module	30	Pure CO_2	1500	1.4	[102]
PVDF-Graphene 1						2.5	
PVDF-Graphene 3						2.5	
PVDF-Graphene 7						2.5	
PVDF	DI water	Lumen	1200	Pure CO_2	20	1.2	[103]
PVDF-MMT 1						1.4	
PVDF-MMT 3						1.4	
PVDF-MMT 5						1.7	
PVDF	DI water	Lumen	n/a	Pure CO_2	n/a	2.0	[105]
PVDF-ZSM5 1						4.0	
PVDF-ZSM5 3						4.5	
PVDF-ZSM5 5						6.0	
PVDF-4%SiO_2-30	1M DEA	Lumen	170	CO_2/N_2 (19/81)	10	1.8	[106]
PVDF-4%SiO_2-50						2.4	
PVDF-4%SiO_2-80						3.1	
PVDF-2%SiO_2-80						2.7	
PVDF	DI water		n/a	Pure CO_2	n/a	0.27	[107]

PVDF-PBI 15 wt%		Flat Sheet Module				0.28	
PVDF-PBI 20 wt%						0.42	
PVDF-PBI 25 wt%						0.15	
PVDF	1M MEA	Shell	690	Pure CO_2	n/a	15	[108]
PVDF-TiO_2-2						6	
PVDF-fTiO_2-1						11	
PVDF-fTiO_2-2						11	
	2M MEA		390			13	
	5M MEA		270			13	
PVDF	1M MEA	Shell	n/a	Pure CO_2	n/a	4.0	[109]
PVDF-fTiO_2-SiO_2-0.5						6.0	
PVDF-fTiO_2-SiO_2-1						8.0	
				CO_2/CH_4 (40/60)		3.2	
CA-m-PVDF	1M MEA	Shell	n/a	Pure CO_2	n/a	2.8	[117]
	DI water					2.3	
ZrO_2 on Al_2O_3 FAS	5 wt% MEA	Lumen	30	CO_2/N_2 (12.5/87.5)	2	1.3	[111]
Al_2O_3 A FAS	DI water	Lumen	660	CO_2/N_2 (20/80)	5	0.78	[84]
			1660			1.3	
Al_2O_3 B FAS			1400			4.0	
					2	7.8	
Al_2O_3 C FAS			920		0.8	2.2	
Al_2O_3 LTS-2	30 wt% MEA	Shell	n/a	CO_2/N_2 (13/87)	8300	2	[113]
Al_2O_3 LTS-4						8	
Al_2O_3 GTS-1		Lumen			5900	1.5	
Al_2O_3 GTS-3						1.5	
Al_2O_3 FAS	1M AMP + 0.2M PZ	Flat Sheet Module	n/a	CO_2/N_2 (9/91)	200	0.3	[114]
Al_2O_3-SiO_2 FAS-1						0.85	
Al_2O_3-SiO_2 FAS-3						1.1	
Al_2O_3-SiO_2 FAS-5						1.1	
Kaolin-Al_2O_3 FAS	DI water	Lumen	64	Pure CO_2	S, n/a	50	[115]
			640			180	
[a] Reynolds number calculated by the present authors from data provided in each paper.							

Table 4. CO_2 stripping properties of the membrane contactors.

	Solvent	Solvent Side	Solvent Reynolds number [a]	Temperature (°C)	Sweep gas Reynolds Number [a]	CO_2 flux (mmol/m^2 s)	Ref.
PEI	1M DEA	Lumen	390	80	30	13	[90]
PEI-PEG400			320			25	
PEI	0.1 M MEA	Lumen	820	80	7	0.16	[91]
PEI-EtOH 2wt%				80		0.21	
			870	85		0.35	
			910	90		0.5	
PEI-EtOH 4wt%			820	80		0.14	
PEI-PA	1M MEA	Lumen	830	60	n/a	10	[92]
			1200	70		17	
			1350	80		19	
PSf	1M MEA	Shell	410	80	7	0.12	[93]
PSf-EtOH 2 wt%						0.2	
					3	0.09	
PTFE	30 wt% K_2CO_3	Flat Sheet Module	2600	60	n/a	2.8	[83]
			3100	80		6.9	
			3500	100		13	
PALL Supor 200R			2600	60		2.8	
			3100	80		8.6	
			3500	100		20	
PTFE	3M MEA	Lumen	64	90	13	0.35	[118]
				100		0.7	
	5M MEA			100		1.3	
PVDF	1M DEA	Lumen	390	80	30	35	[90]
PVDF-PEG400			320			40	
PVDF	10 wt% DEA	Lumen	160	80	n/a	11	[98]
PVDF-LiCl 3%						11	
PVDF-LiCl 5%						16	
PVDF-HFP	10 wt% DEA	Shell	150	80	12	8	[99]
PVDF-HFP-PEG400						9	
PVDF-HFP-PA						10	
PDMS	30 wt% MEA	Shell	500	90-102	n/a	3	[9]
Porous PEEK	8 wt% MDEA	Shell	n/a	104	n/a	18	[116]
PVDF	DI water	Lumen	1500	27	0.07	2.6	[104]
			2100	45	0.06	5.6	
			3500	80	0.05	6.9	
PVDF-MMT 1			1500	27	0.07	3.2	
PVDF-MMT 3			1500	27	0.07	3.6	
PVDF-MMT 5			1500	27	0.07	4.2	
			2100	45	0.06	7.0	
			3500	80	0.05	7.5	

[a] Reynolds number calculated by the present authors from data provided in each paper.

PSf and PEI membranes are commercially available by NIPS fabrication because they dissolve well in common organic solvents. However, they are mostly used for gas separation or water treatment applications. Despite the good thermal and chemical stability of these polymers, their more hydrophilic nature results in membrane wetting when used in membrane contactors, limiting their use in this application. Structural modifications of these membranes have been widely investigated to enhance porosity while maintaining mechanical strength. Modifications to the surface or sub-layer can also improve hydrophobicity and the corresponding breakthrough pressure [90]. For example, introducing additives into the polymer solution or the bore fluid induces instant solvent demixing resulting in a more porous structure [89-94]. Additives such as acetone, ethanol (EtOH), methanol (MeOH), phosphoric acid (PA), glycerol, salts and acids, in different concentrations in PEI increased or decreased porosity and surface pore size and this affected the CO_2 flux [89, 91, 92]. Kianfar et al. similarly showed that the addition of EtOH as a co-solvent with NMP in a PSf solution increased porosity during phase inversion where water was the anti-solvent [93]. The addition of low molecular weight poly(ethylene glycol) (PEG) to an NMP solution of PEI increased the viscosity of this dope solution and this induced a membrane with a more sponge-like structure during phase inversion with water, by delaying the outflow of the solvent [90]. The more sponge-like structure increased CO_2 flux and the breakthrough pressure by enhancing surface porosity and pore sizes. Although the same additives were introduced in the membranes, the properties can be varied due to other fabrication conditions such as polymer concentration, spinneret size, air gap (distance between spinneret and coagulation bath) or the types of bore fluid. For example, the PEI membranes prepared by Naim et al. with water as bore fluid [92] presented much higher average pore sizes and effective surface porosity than other PEI membranes, prepared with the use of similar additives, but with an NMP/water mixture as the bore fluid [89, 91], resulting in much higher CO_2 flux in both absorption and stripping (Tables 3 and 4). The use of water as

both bore fluid and non-solvent led to more rapid phase inversion and thus the formation of fine finger-like voids at both the inner and outer surface of the membrane [92]. Indeed, numerous references describing the effects of preparation conditions on hollow fibre fabrication can be found in the literature [119, 120]. Although the difference in pore structures can appear minimal in microscopy images, the membrane viability for membrane contactor applications is often significantly influenced by impacts on porosity, breakthrough pressure, or contact angles.

Polymers that are less soluble in organic solvents are formed into membranes by stretching and thermal processing. PP, PE and PTFE are examples of the polymers that are the most commonly prepared using this approach [6]. PE and PP membranes have been studied widely for commercial separation processes, despite their low porosity that often limits the membrane performance. Fabrication of PE or PP membranes is generally by thermal processes such as TIPS or melt extrusion due to their low melting points and as such solvent-free fabrication can minimise cost, environmental footprint and contamination risks. For example, Accurel® and 3M Liqui-Cel® are both commercial modules made from PP hollow fibres that have been used for over 20 years for dissolved gas control [85, 121-125]. More recently, post-combustion CO_2 separation applications have been developed with Liqui-Cel® membranes, focussing on the solvent composition, membrane process designs, or membrane surface modifications [126-129]. However, PP and PE membranes can be chemically degraded during long-term operation in contact with an amine-based solvent [22, 130].

PTFE is an attractive membrane material for numerous applications due to its great hydrophobicity, outstanding chemical and thermal stability, and toughness. However, the insolubility and thermal stability of PTFE has complicated the membrane fabrication process. Current fabrication methods include mechanical stretching, spinning, and pore-forming applied to form flat sheets or hollow fibres, as described in Figure 5 [131]. For the mechanical

stretching, PTFE resin is first mixed with a lubricating agent to form a paste, extruded into a sheet at a high temperature and then biaxially stretched to create pores or cracks. The porosity of the membrane by this method varies from 20-70 % with average pore diameters in the range 0.03-1.0 μm [131].

Electrostatic spinning, called electrospinning has been applied to prepare PTFE nanofibres with the desired morphology in high productivity [6]. A polymer solution is injected from a needle onto a substrate through an electric field of high voltage, forming a sheet of nanofibres. Polymers such as poly(vinyl alcohol) or poly(caprolactone) are blended into the PTFE emulsion to aid in the electrospinning. These additives are removed by thermal or chemical treatment after electrospinning and pure PTFE membranes are obtained [132]. Dry/wet spinning of PTFE allows membrane formation as flat sheets and hollow fibres by phase inversion from a PTFE paste or viscous polymer solution. The spinning paste is extruded through a nozzle, then the membrane structures are controlled by stretching and heating downstream. Pore-forming agents such as $ZnAc_2$, NaCl, and $BaCl_2$, are also introduced into the paste, then removed by washing or high temperature calcination after the membrane formation. Tang et al. reported PTFE membrane fabrication with Isopar G lubricant and sintering at 360 °C [133]. This hollow fibre membrane presented a porous structure with a surface porosity of 60 %.

Commercial PTFE hollow fibre membranes with pore sizes of 300 nm and porosity of 50 % have demonstrated a CO_2 absorption flux of 0.5 and 0.9 mmol/m^2 s, respectively, when MDEA and 1DMA2P solvents were used [36]. The same PTFE membranes were also used for CO_2 absorption with blended amine solvents and exhibited a CO_2 absorption flux of 1.15-1.8 mmol/m^2 s, despite operation under a small CO_2 partial pressure [40].

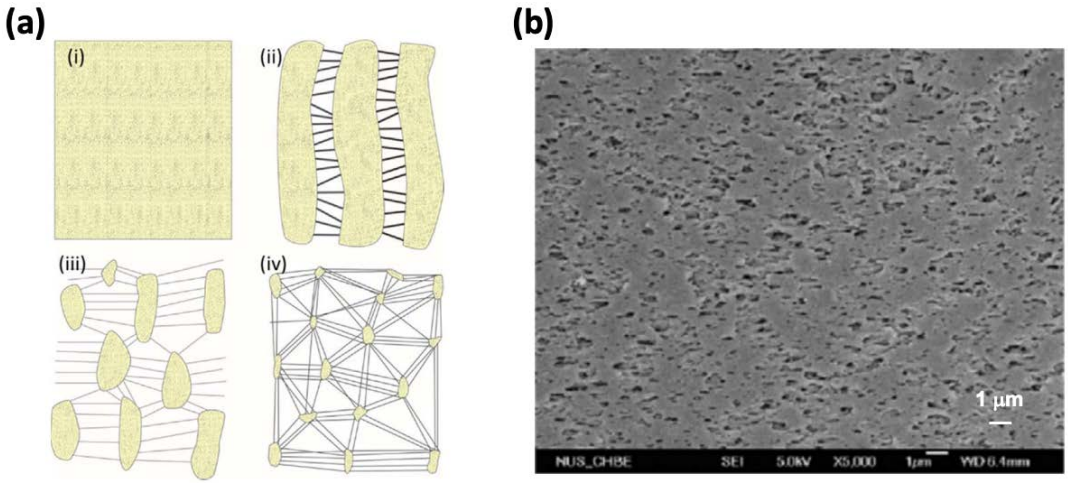

Figure 5. (a) schematic of PTFE stretching process in different stages: (i) raw PTFE sheet, (ii) early-stage stretching or strip crack process, (iii) node-forming stage or uniaxial tension process, and (iv) uniform node connection or biaxial tension process, (b) typical morphology of PTFE membranes formed by such a stretching process. Reprinted with permission from [131]. Copyright 2018 Elsevier.

Amorphous fluoropolymers, such as the Teflon AF series, Hyflon AD or Cytop have been developed as an alternative to PTFE since they can be dissolved in fluorinated solvents, such as Fluorinert FC-40, FC-72, fluorinated Fluid PF-5060, or Novec 7200. These membranes have shown excellent CO_2 permeability, hydrophobicity, temperature stability and chemical resistance and can be an attractive option for membrane contactor applications as a non-porous coating [11, 134-137]. Dip-coating on porous hollow fibre supports can achieve a coating layer thickness of around 1 μm. Dai et al. reported the use of a composite membrane of AF2400 coated on a commercial PP membrane for the separation of CO_2 and H_2 at high temperature and pressure using membrane absorption with IL solvents [137]. Although the dense coating layer of AF2400 brought an additional flow resistance, the ultrathin nature of the layer provided little resistance to the CO_2 transport. The membrane was stable at 20 bar and 80 °C conditions, having a CO_2 flux of 0.37 mmol/m^2 s with the selected IL ([Bmim][TCM]) solvent. The

performance at pressures over 10 bar exceeded that of the porous PTFE membranes. The unique solvent resistance and low water permeability of AF polymers was utilised in the use of AF1600 membranes for CO_2 absorption and stripping using MEA solvent [82, 138]. An AF1600 composite membrane on porous PP presented a higher CO_2 absorption flux than a porous PP membrane since the pore wetting of the PP membrane was severe while the AF1600 membrane stayed dry. There was an initial flux decline during long-term operation, but the AF1600 membrane demonstrated consistent performance over 10 h with an overall mass transfer coefficient of 8 x 10^{-4} cm/s at 50 °C. The overall mass transfer coefficients for other composite membranes formed with skin layers without fluorine functional groups, but with high free volume declined after 5 h because of high water vapor transfer that condensed in the pores. An AF2400 coating of 1.7 μm thickness on porous PP exhibited a similar CO_2 mass transfer coefficient of 7.5 x 10^{-4} cm/s at 25 °C [11].

Hyflon (AD 60X) is another amorphous fluoropolymer similar to the AF series, having great hydrophobicity [139]. When Hyflon was coated on the surface of PVDF after modification, the surface contact angle increased from 126° to 141°. This membrane also presented increased breakthrough pressure, swelling resistance to alcohol and mechanical strength. Despite the excellent properties of the Hyflon membranes, their use in CO_2 absorption or stripping are unreported. Their poor solubility, even in fluorinated solvents, and the high cost of the amorphous fluoropolymers has limited their applications and only a few studies have been reported [134, 140].

The Porogen membranes under development by the Gas Technology Institute (GTI) and Air Liquide are composed of a porous polyether ether ketone (PEEK) onto which a perfluorocarbon polymer is either chemically grafted or coated [141, 142]. As discussed in Section 5.1, these have been tested at pilot scale as a membrane contactor for carbon capture and are also being commercialised for gas separation applications [143].

PVDF is one of the most widely studied membrane materials for membrane contactor applications [86]. PVDF is very soluble in a wide range of organic solvents and has a moderate melting temperature that allows membrane fabrication by NIPS and TIPS. The morphology and properties of the PVDF membranes prepared by NIPS can be varied depending on solution composition and controlled for improved mechanical strength or hydrophilicity. On the other hand, PVDF membranes prepared by TIPS generally show higher mechanical strength and more uniform pore structures [86]. Pang et al. reported that the morphology of PVDF membranes could be controlled by additives in the NIPS process [97]. The addition of non-solvents such as PA and lithium chloride (LiCl) into the dope solution transformed the membrane morphology from finger-like to sponge-like with increased mechanical strength. The additives affected the membrane pore size, surface porosity and breakthrough pressure, enhancing the wetting resistance and the membrane CO_2 flux. Addition of other non-solvents such as PEG, ethanol, or glycerol also resulted in sponge like membrane structures [90, 96]. The sponge-like structures generally provide high tortuosity, so that water cannot easily pass through the pores, resulting in less pore wetting. Generally, the addition of non-solvents to the dope changes the surface pore sizes, where larger pores are advantageous for high CO_2 flux, while smaller pores increase the breakthrough pressure for better anti-wetting properties. In recent years, modifications of these membranes by blending with functional materials or surface functionalisation has also been studied to reduce membrane wetting.

However, the very high hydrophobicity of PVDF membranes is shown to deteriorate with time in membrane contactor applications as the solvent penetrates through the pores, leading to a flux decline due to membrane wetting [80]. Moreover, the morphology of PVDF membranes can change with time due to chemical interaction with amine solvents that leads to polymer degradation [108, 144, 145] As summarised in Table 3 and 4, the majority of the

studies of polymeric membrane contactors for CO_2 separation use such PVDF membranes, but ultimately it is not viable for long term operation with amine based solvents.

In summary, membrane properties including pore size, porosity and contact angle can be controlled by modifying preparation conditions and this can lead to either an increased breakthrough pressure or an enhanced CO_2 absorption and stripping flux. Generally, both cannot be achieved simultaneously, as one requires smaller pores while the latter requires larger ones. Further, improvements in breakthrough pressure often only prevent partial or full membrane wetting for short periods, with the CO_2 flux further declining with time. Incorporation of two or more materials to form composite membranes will be detailed in the following section and these may provide better solutions to the membrane wetting conundrum.

3.2. Modification of polymeric membranes

Modification of polymers through surface coating, surface treatment, introducing organic and inorganic additives, and blending with other polymers has been investigated to overcome the intrinsic wetting problems.

Silica nanoparticles are a typical additive to improve hydrophobicity as they are cheap and can be well-dispersed in organic solvents [146, 147]. The hydrophobic silica sol is prepared from tetraethylorthosilicate and chlorotrimethylsilane, then mixed with polymers such as PVDF in solution, prior to NIPS membrane fabrication. A 3 % silica sol in a PVDF solution eliminated the macrovoids in such a membrane because the silica nanoparticles increased the solution viscosity and thus reduced the solvent and non-solvent demixing rate during phase inversion[147]. The approach also improved the hydrophobicity of the membrane, evidenced by the contact angle increasing from 82° to 126° [147]. The resulting hollow fibre membranes also demonstrated CO_2 separation performance using soybean and moringa based biosolvents

with a CO_2 flux of 0.02-0.15 mmol/m^2 s when a CO_2/N_2 (12/88 mol%) mixed gas was employed. The performance was comparable with PTFE membranes in an MEA solvent [146].

Chen et al. prepared dual-layer PVDF hollow fibres using a triple-hole spinneret [106]. Using this approach, they were able to manufacture a thin, hydrophobic inner layer through the addition of modified silica nanoparticles to the inner dope solution. This approach allows the solvent to flow on the lumen side of the hollow fibres in a membrane contactor application, in contrast to the more common approach where the skin layer is on the outside, meaning that the solvent must also flow on the shell side. As compared to the single-layer hollow fibres, the dual-layer hollow fibres presented much higher CO_2 absorption flux of up to 3.12 mmol/m^2 s while having similar contact angle, breakthrough pressure values and maintaining mechanical strength.

Although PVDF does not have reactive functional groups, defluorination and oxygenation reactions through alkali or plasma treatment can form reactive oxygen-containing functional groups on the PVDF chains [148]. For example, treatment with NaOH or ammonia can functionalise the polymer with hydroxyl groups while plasma treatment with oxygen adds carbonyl groups [149]. The modification options should be carefully chosen since alkali treatment can destroy the main PVDF polymer backbone unless the treatment conditions are carefully controlled. This can lead to an uneven surface and low surface porosity, leading to poor permeability [148, 150, 151]. Plasma treatment is less damaging, but only results in modification of the top few nanometres of the surface and the bulk properties are not changed. This can mean that the surface treatment degrades over time by simple abrasion [149] or by diffusion of untreated polymer chains through cracks in the treated layer [152].

Pang et al. grafted a long chain silane, hexadecyltrimethoxysilane (HDTMS) onto PVDF chains during phase inversion by adding aqueous ammonia and HDTMS to the polymer dope solution before hollow fibre spinning [80]. Hierarchical spherulitic particles formed on

the outer surface of the fibres increasing the surface roughness and thus enhanced hydrophobicity. The CO_2 flux increased from 0.99 to 1.79 mmol/m^2 s during absorption into 1M DEA solvent when 1.5 wt% of HDTMS was included in the polymer solution. This flux increased as a function of the HDTMS content to a maximum at 1.5 wt% then decreased at 5 wt% because the surface pore sizes became too small for CO_2 mass transfer. Such modification by chemical reaction was advantageous as the changes to the PVDF persisted over time.

Other hydrophobic compounds such as multi-wall carbon nanotubes (MWCNTs), or graphene can be easily dispersed in a PVDF matrix, leading to improved CO_2 flux [101, 102]. Hydrophobic MWCNTs embedded in PVDF increased the breakthrough pressure by decreasing mean pore sizes but increasing effective surface porosity. Addition of graphene in PVDF membranes also showed similar increases in CO_2 flux by improving hydrophobicity. As shown in Figure 6, unmodified PVDF membranes demonstrate a dramatic decline in CO_2 absorption flux over time due to pore wetting; the flux is reduced to nearly 20-40% of the original value after 200 h operation. However, the CO_2 absorption flux of these modified PVDF membranes remained at 80-97% of the original value by eliminating this issue.

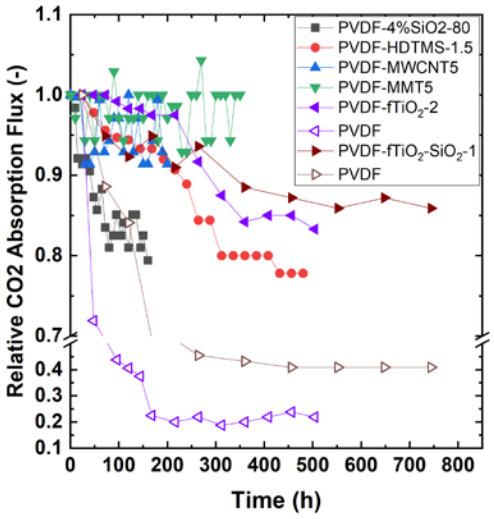

Figure 6. Relative CO_2 absorption flux of modified PVDF membranes as a function of operation time. PVDF-4%SiO_2-80 [106], PVDF-HDTMS-1.5 [80], PVDF-MWCNT5 [101],

PVDF-MMT5 [103], PVDF-fTiO_2-2 (before and after modification) [108] and PVDF-fTiO_2-SiO_2-1 (before and after modification) [109].

Despite the advantages, this is an expensive approach. Inorganic or zeolite nanoparticles, such as montmorillonite (MMT) or ZSM5 with a lamellar layered structure are cheaper additives that enhance the membrane porosity and hydrophobicity, giving excellent wetting resistance in both absorption and stripping processes [103-105] (see Figure 6).

Blending polymers is a convenient method to improve membrane performance, but there are only few reports on this approach in CO_2 absorption applications. Bakeri et al. introduced PVDF into PEI membranes to benefit from the increased hydrophobicity of PVDF and the processability and mechanical strength of PEI [153]. Blending PVDF in small concentrations increased the contact angle from 78° to 84°. This also improved surface pore sizes and porosity, increasing CO_2 flux. However, blending of larger quantities of PVDF induced pore wetting since the pores became too large. Ahmad et al. reported the addition of polybenzimidazole (PBI) into PVDF membranes for biohydrogen production with improved membrane thermal stability [107]. The PBI improved the porosity of the membrane and the hydrophobicity did not reduce significantly when this addition was below 20 wt% [107].

While modifications to the bulk polymer can be effective in improving membrane performance, surface modifications can do so while utilising only a small fraction of the functional materials, which are often expensive. Early studies in this field modified PP membranes by plasma sputtering a PTFE coating [78] or by depositing a porous crystalline polypropylene layer [154]. In another example, TiO_2 was coated onto the surface of a polymeric hollow fibre by immersion in a titania precursor solution, followed by drying and vapor phase hydrolysation. The TiO2/PVDF membranes were further immersed in an ethanol solution containing 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFTS) to form a fluorinated

outer layer that prevented wetting and improved the CO_2 mass transfer [108]. The modification greatly reduced the surface pore sizes within the 1 μm thick fluorinated TiO_2 layer and dramatically changed the hydrophobicity of the hydrophilic TiO_2. The modified membrane exhibited a lower initial CO_2 flux than the neat PVDF membrane since the pore sizes were smaller, but the wetting resistance meant that this performance was more stable (see Figure 6). During the 21 days operation, the CO_2 absorption flux of the PVDF-fTiO_2 membrane with a 1M MEA solution decreased from 12 to 10 mmol/m^2 s. However, the neat PVDF membrane flux reduced from 16 to 4 mmol/m^2 s. The improved chemical resistance also prevented membrane corrosion from the MEA solvent. As shown in Figure 7, exposure to the MEA solvent enlarged the pore sizes in the PVDF membrane by chemical degradation, resulting in membrane wetting, but the surface of the modified membranes was unchanged. A similar approach with a blend of TiO_2 and SiO_2 and a fluorinated outer layer also significantly reduced pore sizes and reduced porosity by blocking large macropores [109]. The schematic image of the TiO_2-SiO_2 modification and the membrane contactor application is illustrated in Figure 8. The surface microstructure was controlled by the amount of silica precursor, building a mesoporous TiO_2-SiO_2 layer on the PVDF substrate. The resulting membranes demonstrated stable performance for 31 days with a CO_2 flux of 8 mmol/m^2 s (see Figure 6).

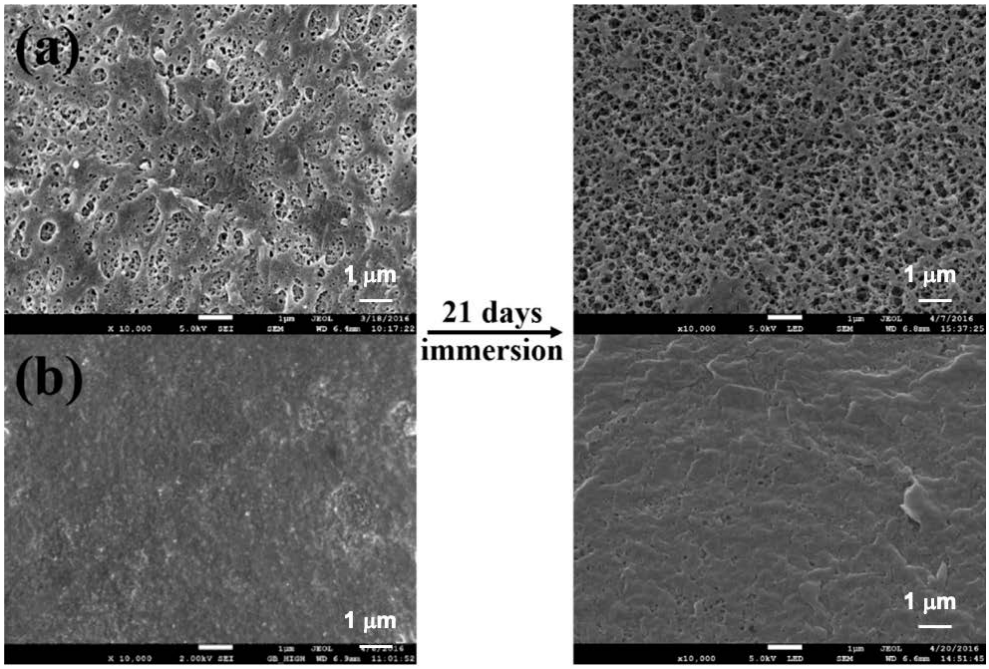

Figure 7. The surface SEM images of (a) PVDF and (b) PVDF-fTiO$_2$ membranes before and after exposure to 1M MEA solution. Reprinted with permission from [108]. Copyright 2018 Elsevier.

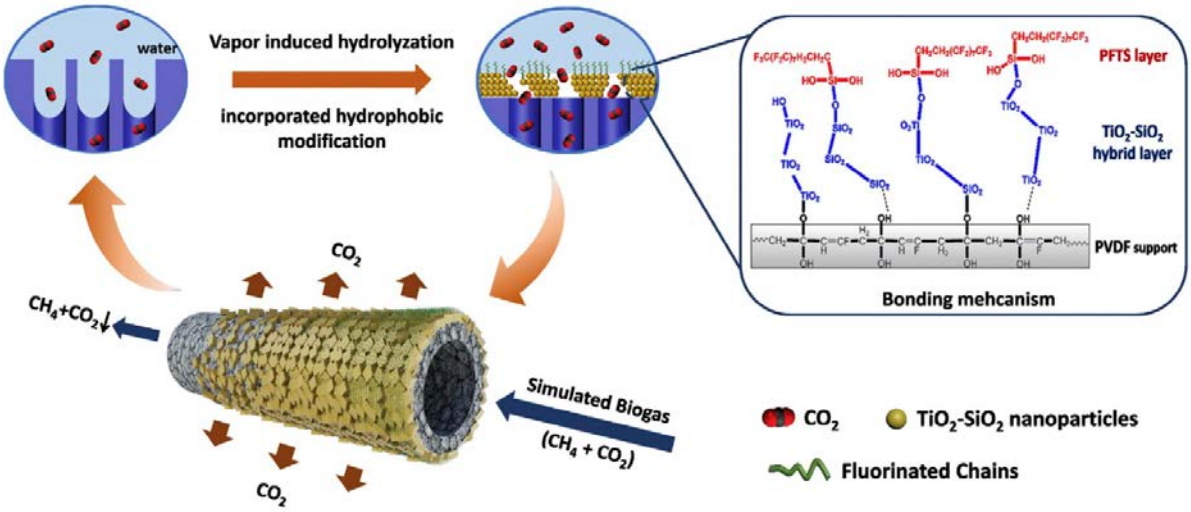

Figure 8. Schematic illustration of the fTiO2-SiO2/PVDF composite hollow fibre membrane and CO_2 removal in a membrane contactor application. Reprinted with permission from [109]. Copyright 2018 Elsevier.

Thin film composite membranes with a non-porous layer on a supporting polymer have been tested with the non-porous layer formed from highly CO_2 permeable polymers such as poly(vinyltrimethylsilane) (PVTMS), poly(trimethylsilyl)propyne (PTMSP), Polymers of Intrinsic Microporosity (PIM) and poly(dimethylsiloxane) (PDMS). The high CO_2 permeability of the dense polymer is essential since it maximises the overall mass transfer. Scholes et al. introduced ultrathin layers of PTMSP, PIM-1 and Teflon AF1600 onto a porous PP support membrane for both CO_2 absorption and stripping with 30 wt% MEA aqueous solution [9, 82, 138]. The CO_2 flux of the composite membranes was lower than the porous membrane without the dense layer, but the decrease was not significant when using PTMSP or PIM-1 since these polymers had high CO_2 permeability due to their large free volume. The overall mass transfer coefficient of the porous PP membrane was very low during CO_2 absorption since the membrane instantly became wet. The initial overall mass transfer of the membranes with a dense layer of PTMSP or PIM-1 was very high, but significantly decreased after 5 h operation (Figure 9). The final value was even lower than that of the wetted PP membrane, meaning that water from the aqueous solution had permeated through the dense layer and accumulated in the pores of the substrate. However, the membrane coated with Teflon AF1600 membrane presented stable performance over time despite having a lower initial flux than PTMSP or PIM-1 (Figure 9). As a perfluorinated polymer, the extreme hydrophobicity of Teflon AF1600 prevented water vapor permeation so that the membrane could provide consistent performance. Despite the relatively short operation time described in this work, thin film composite membranes have been shown to operate stably for several months [9]. Nguyen et al. also reported thin film composite membranes of PTMSP and Teflon AF2400 on a PP support and showed that the membranes withstood contact with amine solutions without degradation and overall mass transfer coefficients that were comparable to the microporous membranes [136].

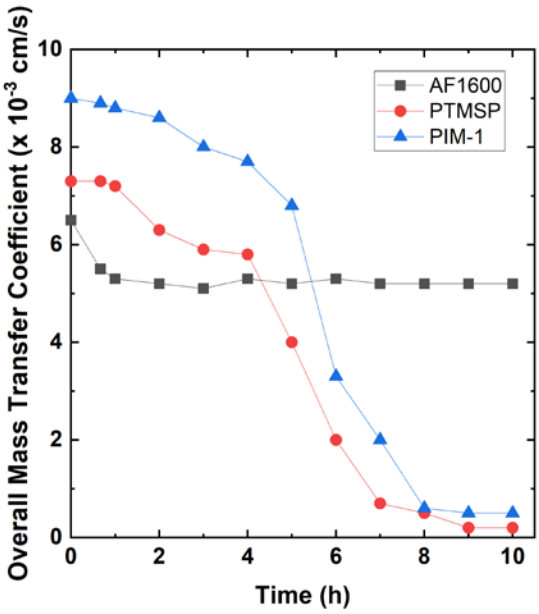

Figure 9. Overall mass transfer coefficient of thin film composite membranes, coated on PP substrates as a function of operation time [82].

In summary, many modification of polymeric membranes have been proposed to reduce pore wetting through increased hydrophobicity. This includes the introduction of nanomaterials within the polymer phase or on the surface. While these methods are effective over short periods, they are often not tested over the long time frames needed for industrial operation and in many cases are likely to be ineffective over these periods due to a gradual loss of these hydrophobic properties. Conversely, thin film composite membranes with a non-porous surface layer can successfully prevent membrane wetting over longer periods, but this approach significantly decreases the CO_2 flux.

3.3. Biocatalytic membranes

The incorporation of biocatalytic carbonic anhydrase (CA) into a surface coating can have the combined benefits of reducing membrane wetting while enhancing the absorption kinetics for solvents such as potassium carbonate. As a naturally occurring enzyme, CA

catalyses the hydration of CO_2 from the gas phase to form bicarbonate ions. The immobilisation to a solid substrate can improve the thermal and pH stability of the enzyme by reducing its conformational flexibility and thus capacity to denature[155]. Yong et al. used a layer-by-layer approach to coat CA onto both PP hollow fibres and PSf fibres with a PDMS coating and showed that this resulted in a three-fold increase in the rate of CO_2 absorption while also reducing membrane wetting [156]. The electrostatic adsorption process was rapid and simple and allowed the CA film to be applied to fibres already assembled within a module. Xu et al. immobilised CA on PVDF after the deposition of polydopamine and polyethylenimine and also found improved CO_2 absorption when using water as a solvent [117]. Free carbonic anhydrase enzymes can be unstable, particularly when employed at the high ionic strength and alkaline pH of capture solvents. Xu et al. showed that the immobilisation of the enzyme improved this stability in a test over 40 days [117]. Yong et al.[157] found the stability of the immobilised enzyme to be highly temperature dependent, with activity retained for up to 80 days at 25^{o}C, but only 4 days at 50 °C in a 30 wt% potassium carbonate solution. Hou et al. reported TiO_2-based biocatalytic membranes by immobilisation of CA onto functionalised TiO_2 nanoparticles, which were in turn coated on PVDF membranes using a sol gel approach. [158]. Immobilisation of CA on TiO_2 could be achieved by physical adsorption or sequential chemical reaction with glutaraldehyde. The physical adsorption approach was simple but did not provide a stable attachment so that the catalytic activity gradually reduced with time. Conversely, sequential immobilisation required a multistep preparation technique but resulted in a more stable system.

Metal organic frameworks material are regarded as a promising immobilisation structure for CA, which can be achieved by surface immobilisation, diffusion into the pores or by in-situ encapsulation [159]. Zhang et al. [160] used a CA/ZIF-L composite mixed with MDEA solution and showed that only 0.05 g/L of the CA/ZIF-L in 1M MDEA was sufficient

to cause a three-fold higher CO_2 absorption rate. When the CA/ZIF-L concentration was increased to 0.5-1.0 g/L, the CO_2 absorption rate was comparable to that of a 1M MEA solution. Ren et al. [161] embedded CA into ZIF-8 nanoparticles and then encapsulated these within a poly(vinyl alcohol) and chitosan hydrogel network. The hydrogel showed much higher CO_2 capture capacity than either the free CA or CA@ZIF-8. While in this case a free-standing membrane was not formed, the immobilisation technique is potentially useful for ZIF-L membrane fabrication.

In conclusion, although CA immobilisation can reduce membrane hydrophobicity, membranes with biocatalytic CA have exhibited improved CO_2 absorption flux and overall mass transfer coefficients for low temperature CO_2 absorption. However, degradation of the enzyme under the harsh conditions of capture solvents results in enzyme de-activation over time, particularly at higher temperatures. Additional studies on membranes with higher CA loading, activity and thermostability are required to meet the requirements for CO_2 separation and CO_2 conversion through a membrane contactor process.

3.4. Ceramic membranes

Despite a greater cost than polymers, ceramic materials offer better structural, chemical and thermal stability, so these membranes have been applied in numerous separation processes [6]. Widely used ceramic materials, such as alumina (Al_2O_3), titania (TiO_2), silica (SiO_2), and zirconia (ZrO_2), are fabricated into flat or tubular membranes by methods such as isostatic pressing, extrusion, or slip-casting with binders and plasticisers, then often sintered to give the necessary porosity with regular pore sizes. Ceramic hollow fibre membranes have been widely studied as these can reduce the weight of the module relative to flat sheet systems [84, 110-115, 162]. Ceramic hollow fibres can be prepared by phase inversion from a solution containing both polymers and ceramic particles. The small concentrations of polymers in the solution

allow formation of the ceramic/polymer mixture into a membrane by NIPS. The polymer phase is then removed by high temperature sintering to obtain pure ceramic membranes. Koonaphapdeelert et al. prepared hydrophobic ceramic hollow fibre membranes from an Al_2O_3/poly(ether sulfone) (PES) solution by phase inversion and then sintering at 1200-1500 °C [110]. Because of the hydrophilicity induced by the hydroxyl groups in the ceramic membranes, surface treatment by fluoroalkylsilane (FAS) coupling was used to change the surface to be hydrophobic, while maintaining the thermal stability of the grafted FAS up to about 250 °C. High temperature sintering at around 1200 °C transformed the Al_2O_3 structure from hydrous γ- or ρ-Al_2O_3 to more anhydrous α-Al_2O_3 by eliminating hydroxyl groups, also reducing the hydrophilicity. The contact angle of the Al_2O_3 hollow fibre membranes after sintering at 1200 °C was 52.5°, while after sintering at 1500 °C, this increased to 83.4°. However, after grafting with FAS, the contact angles increased to 125° and 105°, respectively.

Lee et al. also prepared hydrophobic Al_2O_3 hollow fibre membranes from an Al_2O_3/PES solution [84, 112, 113]. Membrane characteristics such as overall porosity, pore sizes and breakthrough pressure varied depending on the extrusion pressure or rate. Generally, the effective surface porosity and gas permeance of the ceramic membranes was higher than that of the polymeric membranes. Due to the number of hydroxyl groups, the surface of Al_2O_3 was again modified simply by immersing in an FAS solution, as shown in Figure 10 [84], which increased the contact angle to around 120°. These ceramic membranes demonstrated a CO_2 flux of 0.8-8 mmol/m^2 s even with a low solvent flow rate [84]. The flux was varied by changing membrane porosity and pore size, as well as gas and absorbent flow rates. The use of a baffle and distributor within the membrane module also altered the membrane performance [113].

The main drawbacks of ceramic membranes are their high cost, their brittleness, and the high temperatures required for sintering. The use of kaolin clay ($Al_2Si_2O_5(OH)_4$) for these membranes can be advantageous because of its low sintering temperature and ready availability.

Abdulhameed et al. reported a ceramic membrane prepared from kaolin/Al_2O_3 mixed powder with sintering at 1450 °C that was thermally stable up to 270 °C [115]. The crystalline structure of the alumina and kaolin was eliminated after sintering, with the kaolin compounds transformed into mullite ($3Al_2O_32SiO_2$). The membrane exhibited a remarkably high CO_2 absorption flux, compared to other ceramic membranes. The relatively low cost of kaolin also facilitates a competitiveness with polymeric membranes.

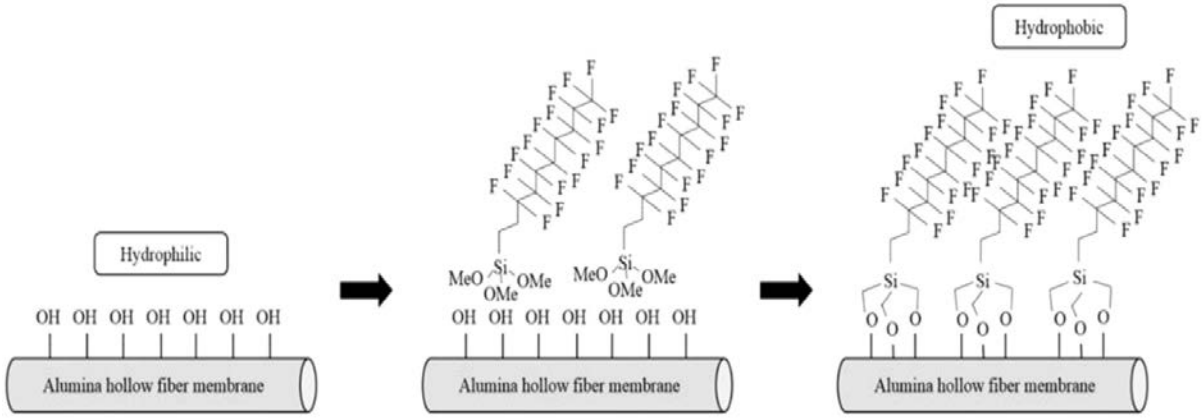

Figure 10. Schematic diagram of FAS coupling to hollow fibre membrane surfaces. Reprinted with permission from [84]. Copyright 2015 Elsevier.

Figure 11. Images of (a) fresh ZrO_2 membrane, (b) ZrO_2 membrane after one month on site operation, (c) fresh PP hollow fibre membranes and (d) PP membranes after one month on site operation. Reprinted with permission from [111]. Copyright 2015 Elsevier.

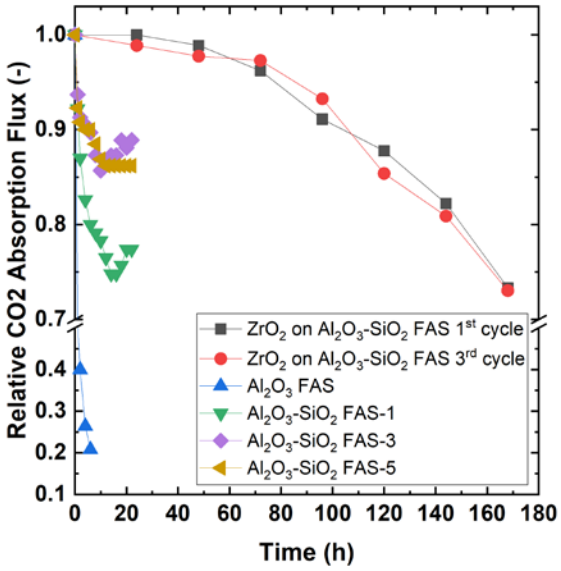

Figure 12. Relative CO_2 absorption flux of ceramic membranes as a function of operation time. ZrO_2 on Al_2O_3-SiO_2 FAS [111], Al_2O_3 FAS [114] and Al_2O_3-SiO_2 FAS [114].

Yu et al. grafted FAS onto a ZrO_2 layer which in turn was applied to an Al_2O_3 support layer [111]. Figure 11 shows these membranes as well as commercial PP porous membranes before and after exposure to a dusty flue gas with a particulate level of 30 mg/m^3 for a month [111]. The PP membranes were fouled by the dust, but the superhydrophobic ZrO_2 membrane was 'self-cleaning' with the dust being removed within condensed water droplets. As described in Figure 12, the CO_2 absorption flux of ZrO_2 composite membranes gradually declined over time due to partial membrane wetting. However, after drying at 60 °C, the membrane demonstrated the same trend in the absorption flux for over 160 h. A significant advantage in this case was that the detrimental effects of wetting in this case could be alleviated by such periodic drying, which was not possible for the PP membranes.

Lin et al. [114] prepared a SiO_2 aerogel layer on the surface of an Al_2O_3 substrate by a sol-gel process. Due to the high porosity and surface area, repeated FAS treatments were

required to provide sufficient hydrophobicity to achieve adequate CO_2 flux. However, the silica layer gave a uniform surface structure that led to a higher CO_2 flux and resistance to wetting than the neat alumina membrane. The membrane performance initially declined when exposed to an amine solvent for CO_2 absorption (Figure 12), but the CO_2 flux recovered to the original level when dry nitrogen was used to remove stagnant amine solvent from the pores. Without the SiO_2 layer, the CO_2 absorption flux declined to 20% of the original performance after 10 h despite the FAS treatment. However, the application of the FAS treatment at least 3 times after coating of the SiO_2 aerogel layer effectively prevented membrane wetting.

In summary, most studies on ceramic membranes have utilised hollow fibre forms to overcome the low effective areas of disc or tubular types. FAS treatments are essential to improve the membrane hydrophobicity. These simple treatments are simple but provide the resilience needed to withstand the operating conditions in membrane contactor applications.

It is obvious from the above discussion, that a vast effort has been dedicated to improving the properties of both polymeric and ceramic membranes to eliminate membrane wetting and to enhance mass transfer. However, a review of Table 3 indicates that for CO_2 absorption the choice of solvent, the allocation of fluids to the shell or lumen side and the Reynolds number of both fluids plays just as important a role in dictating system performance. Similarly Table 4 shows that the stripping temperature, as well as the solvent type, is critical to the efficacy of CO_2 stripping. The following Sections describe how these features can be manipulated.

4. Membrane modules and processes

4.1. Modules

The module configuration greatly affects the membrane performance as it determines the mass transfer resistance of the solvent and gas [6]. The module designs are based on two types of membranes; flat sheet and hollow fibre.

Flat sheet membranes have notable advantages such as ease of membrane fabrication, characterisation and module assembly, and higher flux per unit areas [163]. The characterisation of novel membranes such as electrospun nanofibres or thin film composites can be readily investigated with a small-sized membrane coupon [164, 165]. A number of different manufacturing processes, such as phase inversion, solution casting, sintering, stretching or sol-gel can be used. A plate-and-frame module uses pairs of membranes with feed sides facing each other in a sandwich-like manner [6]. A suitable spacer is placed on each feed and permeate side to allow for unimpeded flow and to prevent membranes sticking together. The membranes are furnished with sealing rings and plates at both ends to build the plate-and-frame stack.

In a spiral-wound module the flat sheets are wrapped around a central collection pipe. Large-scale spiral-wound systems have been installed widely for gas separation and water treatment but are uncommon for membrane contactor applications as there is no capacity for two feed streams. Usachov et al. reported the use of a PDMS spiral wound module of 1.1 m^2 and a PVTMS plate-and-frame module of 0.12 m^2 for removing CO_2 from air for air conditioning [166]. Flat sheet PTFE and PP membrane contactors have also been reported for CO_2 removal with blended amine solvents for experimental and mathematical modelling, allowing characterisation of membrane properties such as porosity, pore sizes and breakthrough pressure [163].

A hollow fibre module consists of a number of hollow fibres with small diameter assembled together in a tubular module. Hollow fibre modules are known to have the largest membrane area per unit volume (i.e., packing density), with the highest packing density of around 36,000 m^2/m^3 achieved when the diameter of hollow fibre is around 100 μm. This higher packing density can however lead to increased pressure drop, particularly in a fouling service where the void volume is occupied by foulants. The packing density of the hollow fibre modules can be increased by reducing the diameter of the hollow fibres, but this increases the pressure drop on the lumen side. The spacing between fibres must be uniform or fluid channelling can be observed on the shell side, leading to a decline in the overall mass transfer [113].

Most hollow fibres are formed by phase inversion and in this case, it is the outside surface that has low porosity. Similarly, any non-porous coating is normally applied to the outside surface. Thus to prevent membrane wetting, the solvent must be applied to the shell side. Having the solvent on the shell side is also useful if it contains viscous or crystalline compounds, such as K_2CO_3, as these solvents can readily block the narrow pathways inside the hollow fibre. For polymers such as PTFE or PP, where phase inversion is difficult, a paste extrusion process can be used to prepare the hollow fibres, but they often have larger fibre diameter. For such hollow fibres that are not asymmetric in cross-section, the placement of the gas phase on the shell side can be advantageous due to lower pressure drops and as the larger outer diameter leads to increased mass transfer area for this phase [113]. Moreover, this configuration is advantageous for cleaning of the membrane surface by back flushing.

For small-scale membrane contactors, the difference between the CO_2 absorption flux obtained in co- and counter-current systems can be insignificant [163, 167] but in most cases, much higher flux is observed in a counter-current flow [113]. However, simple counter-current, or longitudinal flow through hollow fibre modules does not provide even flow distribution on

the shell side for longer lengths, with shell-side fluid channelling reducing the mean fluid residence time[168]. The 3M Liqui-Cel® membrane contactor avoids this issue through the use of a central baffle and distribution tube (Figure 13) [125]. The feed solution flows through the distribution tube and around the baffle to provide a uniform distribution in a crossflow direction on the shell side, while the gas flows through the lumen [113]. A similar approach has been used for ceramic hollow fibres, as shown in Figure 14. The crossflow module has lower packing density to provide adequate space for the distribution tube but the better flow distribution gives more effective mass transfer. In an alternate configuration, the shell side flow distributor sits at the outside of the hollow fibres (Figure 15). This allows for better packing density while having the same cross flow inside the module [112].

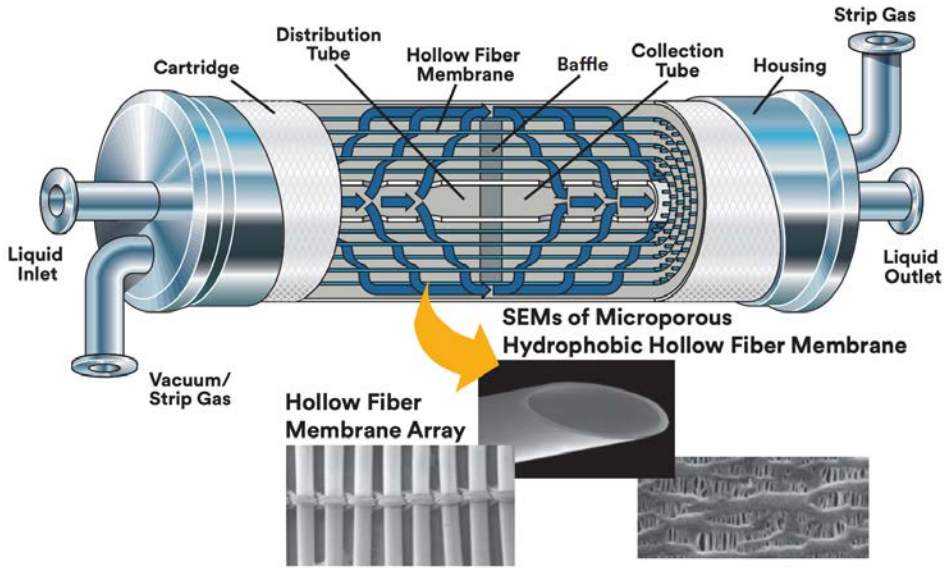

Figure 13. Illustration of the 3M Liqui-Cel® membrane contactor. Reprinted from [125].

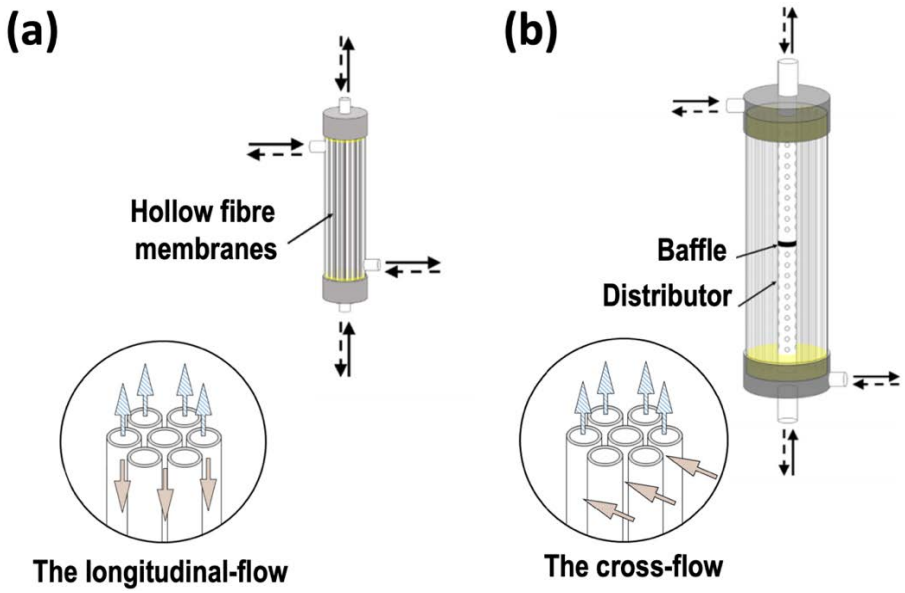

Figure 14. Different configurations used in hollow fibre modules (a) the basic counter-current module with longitudinal flow on the shell side (b) an advanced approach with a baffle and distribution tube providing cross flow on the shell side. Reprinted with permission from [113]. Copyright 2019 Elsevier.

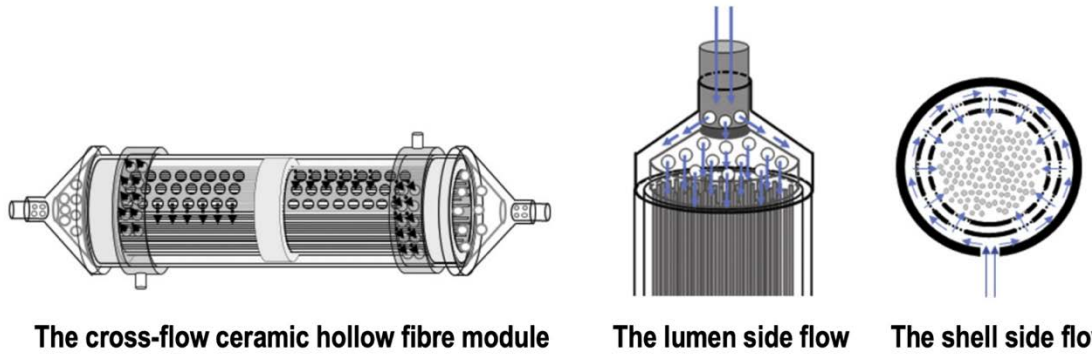

Figure 15. The advanced cross-flow membrane contactor modules. Reprinted with permission from [112]. Copyright 2020 Elsevier.

The glues or adhesives used to seal the modules must be carefully considered as failure most often occurs at the interface between the adhesive and membrane or housing [169]. For most polymeric membranes, adhesives prepared from thermosetting resins are used that require chemical cross-linking by curing agents, heat or other activators after application. Epoxy or

polyurethane based adhesives are most widely used in both laboratories and industry [170, 171], while acrylic, polyaromatic or silicon adhesives can also be used with specific membrane materials. Many of these adhesives however, are not resistant to amine solvents and this can lead to the modules rapidly falling apart. Superhydrophobic materials such as PTFE or FAS coated ceramic materials also require careful selection of an adhesive that is capable of wetting and bonding to these materials. The relatively low surface energy of polyurethane adhesives can effectively wet these hydrophobic materials, penetrating porous substrates for strong mechanical interlocking, but they do not have high temperature resistance, so can only be used for absorption operations below 100 °C. If operation of the module at high temperature will be required, an adhesive that retains strength under these conditions must be used. For example, adhesives prepared from ceramic binders such as alumina, zirconia, silica or graphite, and selected reinforcing fillers can withstand temperature over 1,000 °C. These adhesives play a vital part in module fabrication and endurance but commercial membrane manufacturers rarely reveal their composition. There is a key need for further understanding of these adhesives and how alterations to their composition can be made to provide greater solvent resistance.

4.2. Processes

The overall performance of membrane contactors in CO_2 flux, recovery, purity and energy demand, depends on parameters such as the flow rate, temperature and module arrangement. Resistance to mass transfer occurs through three regions, the liquid phase, the membrane phase and the gas phase, known as the resistance-in-series model [7]. As described in Figure 16, the overall mass transfer resistance through a membrane with fully or partially solvent filled pores is higher than a membrane with gas filled pores due to a higher membrane resistance. The resistance in the liquid phase is reduced due to the chemical reaction that occurs between CO_2 and the solvent, which reduces the dissolved CO_2 concentration to a low value.

This increase in mass transfer is characterised mathematically through an enhancement factor. Operational parameters such as the gas and liquid flow rate influence the mass transfer mechanism by changing the thickness of the boundary layers, while changes to the concentration or partial pressure of the feed influence the mass transfer driving force and the tendency to wetting.

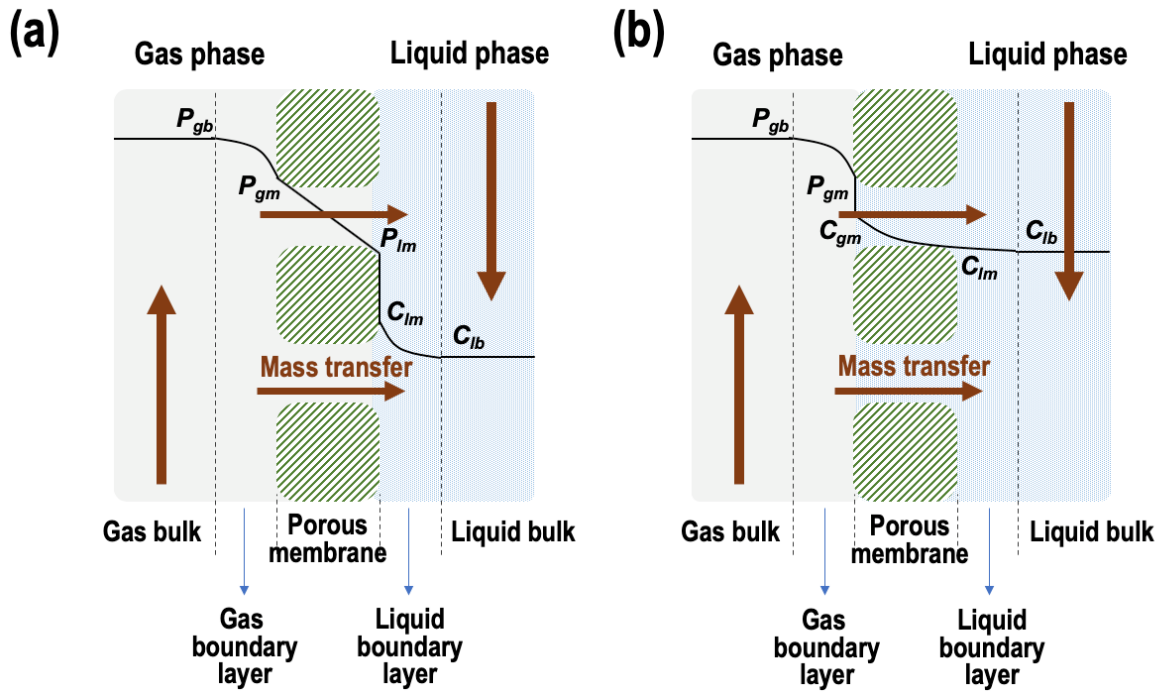

Figure 16. Mass transfer mechanism through a porous membrane in (a) non-wetted mode (with gas filled pores), (b) wetted mode (with liquid filled pores). *P* and *C* are the gas partial pressure and liquid concentration, respectively. The subscripts *gb*, *gm*, *lm* and *lb* represent gas bulk, gas-membrane interface, liquid-membrane interface and liquid bulk, respectively.

The highest CO_2 fluxes are obtained at higher gas and liquid flow rates, as the thickness of the boundary layers are decreased [6, 82, 138, 172-174]. However, this is not the case if it is the membrane resistance that dominates mass transfer, due to either membrane wetting or the use of a non-porous coating [82]. The temperature of the system is also important in both

CO_2 absorption and stripping since it affects both mass transfer and the reactivity between CO_2 and the solvent. Although the mass transfer coefficient for absorption is increased at high temperature due to lower liquid viscosities, the solubility of CO_2 in the solvent generally declines and solvent evaporation increases. The absorption temperature for most solvents is usually controlled between 10-50 °C to balance these competing effects [175].

For CO_2 stripping, higher temperatures enhance the desorption of CO_2, but increase the energy demand, particularly that related to the latent heat of solvent and water vaporisation. A particular advantage of membrane contactors over column stripping operations is that the solvent does not need to completely vaporise, which significantly reduces the total energy demand [173]. For amine solvents, a sufficient partial pressure of CO_2 in the gas phase can be generated at operating temperatures around 80-100 °C, whereas temperatures of 110-130 °C are required in the reboiler of a stripping column[10].

The pressure applied on both gas and solvent flow should be well-controlled for stable performance [175-177]. The solvent pressure must remain higher than the gas phase to prevent bubbling, but if the difference exceeds the breakthrough pressure then membrane wetting occurs. For some applications such as syngas or natural gas treatment, a high feed gas pressure is needed, but the liquid pressure should be similarly increased to maintain this difference [178]. In large scale applications, this can be particularly difficult to achieve during the start-up of the unit and during process upsets. During the start-up procedure of a standard power plant for example, valves are manipulated to stabilise the temperature and pressure of the boiler that will cause significant fluctuations in flue gas pressure and subsequently in the contactor liquid/gas pressure difference [179]. Similarly, in natural gas processing, the feed gas may be at 60 bar, while the contactor differential liquid/gas pressure must be retained at around one bar, meaning that even a 5% shift in feed gas pressure during a process upset would cause membrane wetting. Once the membrane is wetted during such an incident, it is difficult for the situation to be

recovered and so mass transfer remains inhibited [176]. To exacerbate these issues, in full scale membrane units there will also be a longitudinal pressure gradient, so the pressure differential at one end of the contactor will always be much smaller than at the other end [176].

To enhance the mass transfer through the boundary layers, turbulence promoters or additional mixers can be employed. Membrane spacers that promote turbulence are standard within spiral wound modules [180]. The pulsation of solvents in a pulsed sieve-plate column [181], gas bubbling in membrane bioreactors [182] and the use of ultrasonic pulsation [183] in ultrafiltration all increase the flux by thinning the boundary layer and increasing the mechanical shear at the wall. The use of an oscillating flow within the solvent or gas phase of membrane contactors has also been shown to increase the CO_2 flux [184, 185]. In the solvent phase, oscillation with high frequency and amplitude thinned the liquid boundary layer and enhanced the liquid-phase mass transfer coefficient [184]. Similarly, the CO_2 flux was increased by oscillation of the gas phase flowrate, but the effect of frequency was minimal [185].

5. CO_2 absorption and stripping applications

CO_2 removal by packed column absorption and stripping has been widely used for many decades for natural gas, hydrogen, and other gases with low oxygen content. The original trials of this approach using a membrane contactor focused on the absorption of CO_2 from a natural gas stream and from a gas turbine exhaust [186, 187]. However, most studies since that date have focused on the use of membrane contactors for post combustion CO_2 capture from power plants to mitigate global warming [188]. Industrial applications for the membrane contactor process also include acid gas removal and dehydration of biogas, natural gas, and fuel gas mixtures [189]. More recently, CO_2 removal from industrial sectors, such as fertiliser production, steel and plastic production, cement kilns, and syngas has been a subject of investigation.

5.1. Post Combustion Capture

Post combustion CO_2 capture from power plants is the most actively researched area for membrane contactor processes. The flue gas from the combustion generator contains a low concentration of CO_2 at low pressure and this low CO_2 partial pressure means that separation methods such as gas separation membranes and pressure-swing adsorption require additional energy for compression [188]. Solvent-based separations operate effectively at low partial pressures, so have an advantage. While amine scrubbing by column contactors has been the dominant solvent-based approach due to its technological maturity [190], membrane CO_2 contactors have also demonstrated their potential, evidenced by successful commercial application in industry. Pilot-scale demonstrations have been conducted over several decades using commercial hollow fibre membrane modules and lab-scale research has continued to develop novel materials and processes.

The CO_2 capture pilot trial using membrane contactors developed by Gas Technology Institute (GTI) and Air Liquide Advanced Separation (ALaS) is one of the largest pilot plants installed at the National Carbon Capture Canter (NCCC) in the United States. The Porogen hollow fibre membrane modules have been installed in the 0.5 MW scale pilot plant and the system continuously operated for over 600 h in CO_2 adsorption [116, 141, 191, 192]. Practical operation factors such as the use of different solvents, were evaluated at the laboratory with a flue gas containing the contaminants O_2, NO_x and SO_x. These contaminants were shown to have little impact in these laboratory studies, with stable operation and consistent CO_2 capture performance. The membrane contactor system achieved a volumetric mass transfer coefficient of 1.7 s^{-1}, which is around 20 times higher than the mass transfer coefficient of a packed column, and 90 % CO_2 capture rate with 95 % CO_2 purity in one stage. The economic evaluation indicated a 56 % increase in the levelized cost of energy due to the capture operation when a K_2CO_3 solution was used as solvent. This was much lower than the amine absorption

technology (85 % increase) but still higher than the target (35 % increase) [141]. The target could be met by further development to improve the intrinsic CO_2 flux of the membranes, reduce the membrane cost, implement advanced solvents and use a membrane contactor for the stripping step.

In the pilot operation with a commercial 8-inch module of membrane area around 100 m^2, the mass transfer coefficient of the membrane contactor increased to 2.0 s^{-1} with 98 % CO_2 purity [116, 191, 192]. CO_2 absorption flux and removal rate however declined with time due to water vapor condensation in the membrane pores and particulate fouling in the fibre bores [191]. The foulants were found to be rust particles due to the use of carbon steel in upstream equipment, calcium sulfate from the upstream flue gas desulphurisation system and sodium sulfate from the pre-scrubber system [191][193]. This fouling was reduced by the addition of 0.01 and 1 micron filters upstream of the membrane unit and a mesh pad before the membrane itself. However, this decreased the feed gas pressure available for membrane separation [191].

These membranes have also been tested for CO_2 stripping in field trials in a coal-fired power plant in Romeoville, IL. The solvent in this case was 40 wt% activated MDEA with a CO_2 stripping rate as high as 18 mmol/m^2 s for a rich solvent with a 8 wt% CO_2 loading at a stripping temperature of 104 °C and pressure 3.4 Bar gauge [116]. Three stripping strategies were further investigated at the laboratory scale [194]. The use of a steam sweep gave a CO_2 stripping rate of 3.2 mmol/m^2 s. Alternatively, compressing the feed solution to 3.4 Bar gauge pressure, while maintaining the gas side pressure at atmospheric, gave a CO_2 stripping rate of 18 mmol/m^2 s when the feed solution was applied to the shell side at 104 °C. Applying the feed solution to the lumen side of a modified module with a temperature of 121 °C gave the highest stripping rate of 26 mmol/m^2 s.

Post Combustion pilot plant trials of gas absorption using three different commercial hollow fibre membranes were conducted by CO2CRC in Australia at a Victorian brown coal

fired power station [176]. In lab-scale operation, the PTFE membranes exhibited mass transfer coefficients a factor of four greater than the PP membranes with only minor pore wetting. However, in the pilot trial, significant pore wetting was observed for both PP and PTFE porous membranes since the fluctuating gas pressures of the flue gas affected the trans membrane pressure, leading to solvent breakthrough. The non-porous PDMS contactor presented the lowest overall mass transfer coefficient in laboratory studies, but the dense PDMS layer prevented membrane wetting at pilot scale, so that this membrane performance was maintained, giving greater operational stability. There was clear evidence of fly ash buildup at the gas side entrance to the pilot plant PP contactor after only 60 hours of operation, but this did not affect the gas side pressure drop or membrane flux. This may have reflected the use of electrostatic precipitators, a direct contact cooler, and separator upstream of the membrane unit which prevented most ash particles from reaching the contactor. In a separate study, Alharthi et al. [195] showed that such fly ash fouling only reduces CO_2 flux when liquid water is also present. For flue gases derived from bituminous coals, the CO_2 flux can be recovered once this water is removed. However, for lignites with a high calcium oxide concentration, the formation of cementitious by-products leads to a permanent loss of flux.

A similar approach was employed at the Vales Point power plant in Australia for both CO_2 absorption and stripping processes with the same non-porous PDMS membranes [9]. The measured CO_2 absorption flux was stable with a CO_2 recovery of 90 % for 28 days, without membrane degradation or solvent loss. The overall mass transfer coefficient only decreased from 0.09 to 0.08 cm/s during this period. This change was attributed to solvent dilution due to both water vapor transfer into the solvent and MEA vapor transfer into the vapor during stripping. The overall mass transfer coefficient during CO_2 stripping was higher at 0.4 cm/s (a volumetric coefficient of 2.9 s^{-1}) because of the high temperature operation at 90-102 °C. A steam sweep was used to reduce the CO_2 partial pressure in the gas phase.

Vogt et al. [196] considered a two-stage membrane contactor with porous PP membrane modules and showed that this approach exhibited comparable performance with a column with structured packing in a pilot plant with 2.500 Nm^3/h of a model feed gas (14 vol% CO_2, 6 vol% O_2, balance N_2) and 2.000 kg/h MEA solvent. However, they confirmed that PP membranes are unsuitable for use with MEA solvents due to a loss of hydrophobicity over time.

Ceramic hollow fibre membrane contactors have also been tested at large scale with a simulated flue gas [112]. The feed stream contained water vapor and O_2, but the effect of NO_x and SO_x was not reported. The laboratory-prepared module with 200 hollow fibres was used at a flow rate between 0.5-1.0 Nm^3/h for absorption, with a CO_2 capture capacity of 90 % and removal efficiency of 85 %. Volumetric mass transfer coefficients of 0.15-0.5 s^{-1} were observed depending on the feed flow rate and the CO_2 loading in the MEA solvent. The membrane performance fell when the feed flowrate increased, but the CO_2 removal efficiency was maintained. The hydrophobicity of the ceramic membranes and the CO_2 flux were retained after 60 h continuous operation [1].

5.3. Syngas and Hydrogen Production

Syngas is a mixture of carbon monoxide (CO) and hydrogen (H_2) with some CO_2. Small quantities of CH_4, vapor, and heavy hydrocarbons can also be present and in air-blown gasification of brown coal, the syngas is diluted by the presence of N_2 [197]. The gasification processes used to make this syngas from coal, natural gas and biomass were developed many decades ago. However, the use of these processes is increasing due to their ability to produce hydrogen for both combustion to produce electricity or to drive transport within fuel cells; while capturing CO_2. Generation of hydrogen from such fossil fuels is still relatively cheap in comparison to electrolysis of water using renewable energy and if the CO_2 can be captured effectively, the associated greenhouse gas emissions can be reduced significantly. Syngas is

usually converted into CO_2 and H_2 at high temperatures and pressure by the water gas-shift reaction. The CO_2 is then removed. It is advantageous to separate this CO_2 at the high temperatures used for the water gas shift, as energy is not lost to cooling. For this reason, non-volatile solvents such as ILs have been tested in membrane contactors with thermally stable polymer membranes [198, 199].

5.4. Other potential applications

Biogas production from anaerobic digestion of agricultural and food waste has attracted attention in recent years as a source of renewable energy, or as a feedstock for chemical industry [124, 200-202]. Biogas purification also involves CO_2 separation from CH_4 and technologies including solvent absorption, pressure swing adsorption and gas separation membranes have been commercialised for this purpose. Membrane contactor technology can provide the high performance and reduced energy costs of a solvent absorption process while eliminating the issues of emulsions, foaming and flooding. Usually the raw biogas contains 30-70 % CH_4 in and 25-55 % CO_2 in depending on the source, with small volumes of vapor, H_2S, O_2, H_2, N_2 and NH_3 as impurities [201]. When the feed biogas is above atmospheric pressure a high removal rate and efficiency can be easily achieved by employing advanced membranes and solvents.

Other CO_2 emissions from industry arise from the production of coke, steel, cement, plastics and fertilisers. In 2018, the CO_2 emissions from such non-energy use was 11 %, significantly lower than the CO_2 emitted from the combustion of fossil fuels, but still of concern [2]. Cement production from limestone is one industry where the CO_2 emissions are relatively easy to capture, as the concentration is 22-28 vol% [203, 204]. In the steel industry, the CO_2 emissions come from reduction of the iron ore using coal as a reductant, resulting in a feed gas stream that includes N_2, H_2, CO_2, CO, and CH_4 at high temperature [205]. The small footprint

of membrane contactors means that they also have potential for removal of CO_2 within air conditioning systems related to crowded public spaces where levels above the ambient concentration can have a health impact. A novel application explored by our own team is the use of a membrane contactor as a device to simultaneously strip CO_2 from a solvent and to deliver it to microalgal cultures [206, 207]. Such applications can provide future opportunities for these systems.

6. Conclusions and outlook

This review has focused on the latest research trends in both materials and solvents for membrane contactor use in CO_2 absorption and stripping. These devices have become a promising alternative to traditional packed columns primarily because of their small footprint and lower capital cost. However, the use of membrane contactors for CO_2 stripping also offers the opportunity to reduce energy costs, as they can operate below the boiling point of the solvent. While there is a very large body of research devoted to the pore wetting issue with these contactors, this problem is yet to be resolved, particularly for high pressure operations and where pressure fluctuations occur during startup and process upsets. Pore wetting causes an irreversible decline in CO_2 flux during long term operation since the solvent is very difficult to remove once it enters the pores due to the strong capillary forces. The use of a non-porous skin layer on the membrane surface can reduce the issue of pore wetting but also reduces CO_2 mass transfer rates. Further, water vapor can still permeate through the non-porous barrier and condense within the porous substructure.

Much of the research to date has been focused on membrane absorption, rather than stripping. This is concerning, given that there is more potential for energy savings within the stripping system. The membrane properties required for stripping are similar to absorption, but importantly, the system must be resilient to operation at temperatures above 100^oC. More

investigation is required to identify both suitable membrane materials and adhesives that can operate at these temperatures.

Pilot plant trials using commercial polymer membrane modules have also tended to focus on CO_2 absorption rather than stripping. These trials have demonstrated stable performance for post-combustion CO_2 capture but issues have been identified with fouling by particular impurities in some cases. For commercialisation, factors beside the membrane performance, such as the pre-treatment of the feed to remove these particulates, or the provision of better pressure control, should be investigated to ensure a sustainable operation. The optimised design of membrane modules and more pilot scale assessment can reduce the cost of the overall process and extend the application to other CO_2 emission sources. There are significant opportunities for membrane contactors to be applied to ambient air control, to the delivery of CO2 to algal cultures and greenhouses and to cement and steel production processes.

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