

# Hollow Fiber Contactors with Improved Hydrophobicity for Acid Gas Removal: Progress and Recent Advances

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## ABSTRACT

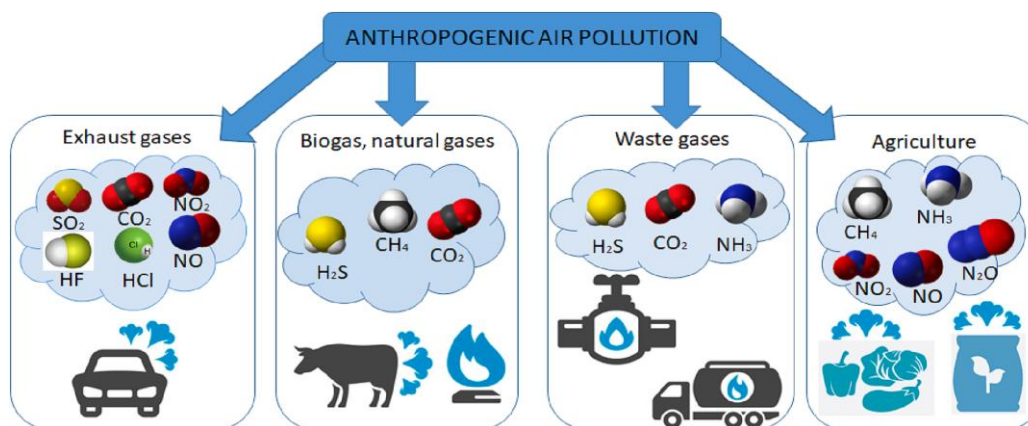
The gas–liquid membrane contactor technology, which integrates the absorption process with membranes, is a developing membrane technology that is especially pertinent to acid gas absorption. When it comes to removing acid gases from natural gas or after combustion, membrane technology has demonstrated potential as a substitute for conventional absorption columns. The membrane contactor offers exceptional operating flexibility and a high mass transfer area. In addition to summarizing the key elements of membrane materials, absorbents, and membrane contactor design, this paper presents the working principle and wetting mechanism of hollow membrane contactors and focuses the most recent advancements in membrane contactor research in gas separation from gas mixtures. The state-of-the-art overview of highly hydrophobic microporous membranes is presented after a discussion of the main challenges to the preparation of superhydrophobic membranes.

*Keywords:* Membrane absorption, hollow fiber contactor, acid gas removal, superhydrophobic membrane, polymeric membrane

## 1.0 INTRODUCTION

Anthropogenic activities have resulted in the production of a wide spectrum of air and water contaminants due to rapid industrialization, continual resource usage, and exponential population growth. The gaseous contaminants are illustrated in Figure 1 from different sources [1].

- exhaust gasses, which include  $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{HF}$ , and  $\text{CO}_2$ ;
- $\text{CO}_2$ ,  $\text{H}_2\text{S}$  - from the processing of natural gas, biogas, and waste dump gas;
- waste gases, which produce  $\text{NH}_3$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{S}$ ;
- Agriculture produces  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{NO}_x$ , and  $\text{CH}_4$ .



**Figure 1** Various gaseous pollutant sources-An Overview [1]

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One of the primary topics that needs to be addressed is the biggest obstacles resulting from the relief of environmental problems. Excessive emissions of air pollutants have detrimental effects on human health as well as a range of environmental consequences. The majority of greenhouse gas emissions globally are attributed to CO<sub>2</sub> emissions from power plants and operating facilities that burn fossil fuels. Additionally, air pollutants that are mostly formed from chemicals containing sulfur or nitrogen can cause major environmental problems including haze and acid rain [2]. Therefore, in order to comply with strict environmental emission limitations or for operational reasons, acid gasses must be removed from the gas stream. There are a number of technologies exists for the removal of acid gasses, including membranes, cryogenic distillation, pressure and temperature-swing adsorption using different solid sorbents, and absorption using solvents or solid sorbents. Of them, solvent absorption appears to be the most promising due to its great selectivity, large capacity, and simple solvent regeneration [3]. Even though absorption is a well-established process that uses packed columns traditionally, there are some drawbacks to this method, including the difficulty in accurately estimating the gas-liquid mass transfer area and the limited range of gas and liquid flow rates that result from operational issues like flooding, loading, channeling, and foaming [4, 5].

The gas-liquid membrane contactor is a established technology that has been used for a very long time to remove acidic gases, particularly CO<sub>2</sub> from post-combustion facilities and the petrochemical industry [6]. Published papers [7] have revealed that membrane contactors have the potential to be one of the most advanced environmental remediation technologies because of its

many advantages. Because of their enormous surface area per apparatus volume, hollow fiber membrane contactors for industrial use which use polymeric membranes and offer the desired compactness and modularity [8]. When a membrane contactor replaces a traditional absorption column as the absorber, the dimension of apparatus can be lowered by 70%. No dispersion between two phases is another significant advantage of membrane contactor hence the separation of the phases in output and foaming in liquid phase can be avoided. It has been possible to fabricate a commercially viable membrane contactor with the use of porous polypropylene (PP) membranes as the fiber. The purpose of this unique membrane contactor's design is to facilitate mass transfer in gas-liquid systems. The important system problem of membrane wetting is not resolved by the membrane contactor's efficiency and simplicity. As the name suggests, membrane wetting is a phenomena in which liquid absorbents pierce the membrane and get wet inside the membrane pores. This means that when the mass transfer efficiency in the membrane module is greatly decreased, a sharp rise in membrane resistance and a decline in absorption performance are seen [9, 10]. Furthermore, a number of surface and structural properties of the membrane, including its roughness, porosity, surface hydrophobicity, pore size, and solvent resistance, influence membrane wetting [11]. Importantly, surface roughness often decreases the tendency of wetting by increasing the membrane's hydrophobicity. It's interesting to note that membranes with higher porosity and larger pores typically experience more severe pore wetting. The proper application of membrane contactors depends critically on the vapour-chemical characteristics of membranes as well as material

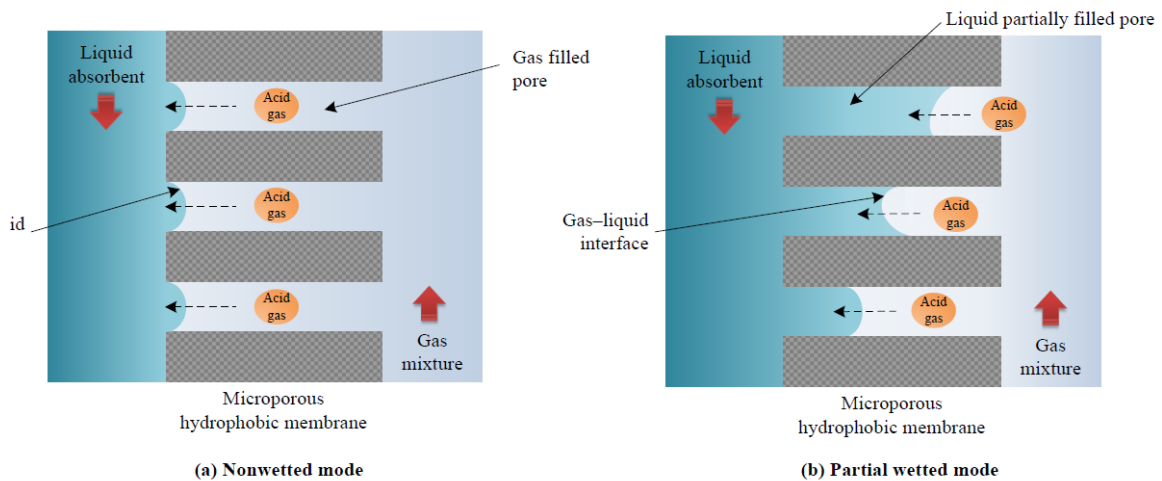
selection and modifications. Using 1-Ethyl-3-methylimidazolium ethylsulfate [emim][EtSO<sub>4</sub>] as an absorbent, Qazi *et al.* [12] have recently investigated the application of hollow fiber contactor coupled with ionic liquid for CO<sub>2</sub> absorption from CO<sub>2</sub>/N<sub>2</sub> mixture.

The purpose of this review paper is to provide a concise summary of the most recent developments in gas-liquid membrane contactor technology, with a focus on potential applications in the removal of acid gases. A summary of the main challenges being addressed for the development of membrane contactors is also included, along with the state-of-the-art review of new membranes, liquid absorbents, and membrane module design and process requirements. We have also focused on the prospects for future developments in membrane contactor technology that could lead to a wide range of practical applications.

## 2.0 ACID GAS REMOVAL BY GAS-LIQUID MEMBRANE CONTACTOR TECHNOLOGY

### 2.1 Basic Principle of Proposed Process

The gas-liquid membrane contactor is related to gas absorption and is an integrated method of membrane separation and conventional absorption. In this technology, membrane acts as a support to keep the liquid and gas phases in contact and promote mass transfer between them [13]. In this kind of setup, a membrane with hollow fiber configuration is preferentially used for this application [5, 14-16]. According to published reports, the specific surface area of hollow fiber modules is considerable, ranging from 1500 to 3000 m<sup>2</sup>/m<sup>3</sup>, while that of traditional contactors is between 100 and 800 m<sup>2</sup>/m<sup>3</sup> [5, 7, 16].



**Figure 2** Scheme of hydrophobic membrane-based gas-liquid contactor, (a) nonwetted mode (b) partial wetting mode [119]

Figure 2a illustrates the process mechanism of the gas-liquid membrane contactor. One side of the membrane allows gas to pass through, and the other allows absorbent liquid to pass through. As a result, in the nonwetted mode, the solute gas absorbs into the liquid

solvent by diffusing over the membrane and generating mass transfer. Remarkably, hollow fiber membranes can function in two different ways: in a wetted mode (absorbent liquid-filled pores) or in a nonwetted mode (gas-filled pores) [17]. In this way, the latter

employs a hydrophilic membrane, whereas the former uses a hydrophobic one. However, due to the lower resistance to mass transfer resulted from the nonwetted mode is preferentially used [17, 18]. The absorbent liquid provides the desired component, even though the applied membrane is a non-selective barrier. As a result, in terms of the capacity of solvent to absorb acid gases and ease of regeneration, it is similar to the conventional absorption process. In this system, solvents that are physical, chemical, or mixed-solvents can all be employed [19]. Because monoethanolamine (MEA) can absorb CO<sub>2</sub> at low partial pressures, it is a cheap chemical solvent that is often employed for CO<sub>2</sub> absorption. Studies on a range of absorbents have demonstrated that MEA is a superior solvent in terms of CO<sub>2</sub> removal efficiency when compared to other absorbents such as methyl-diethanolamine (MDEA), distilled water, and 2-amino-2-methyl-1-propanol (AMP) [20, 21]. But, given the energy needed for regeneration, AMP may be a suitable option among these solvents [21]. On the other hand, MEA degrades when SO<sub>2</sub> and O<sub>2</sub> are present [3]. Ammonia was utilized as the solvent in a study by Resnik *et al.* [22] to concurrently extract CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>x</sub> from exhaust gas. Ammonia offers the advantage of a single procedure in addition to a loading capacity that is three times greater than MEA. Compared to CO<sub>2</sub>, systematic research into the removal of other acid gases like H<sub>2</sub>S and SO<sub>2</sub> is less common. As can be observed from the published study, high SO<sub>2</sub> removal efficiency over 80% was achieved by using aqueous solutions of NaOH and Na<sub>2</sub>SO<sub>3</sub> [23]. Considering the important criteria, surface tension and chemical compatibility with the membrane material are two significant factors that have evolved in membrane contactors

with regard to solvent selection [13, 24]. The fact that a solvent with a lower surface tension is more likely to wet the membrane is an important observation by authors [25]. However, employing a solvent with poor compatibility may lead to a degeneration of the membrane structure and an increase in membrane wetting [26].

## 2.2 Membrane Wetting

A resistance of membrane to wetting is typically indicated by  $\Delta P$ , or breakthrough pressure, which is determined by the Young-Laplace equation (Eq. 1) and is also referred to as liquid entry pressure, or LEP [7, 10, 12]:

$$\Delta P = -\frac{2B\gamma\cos\theta}{r_{max}} \quad (1)$$

where  $r_{max}$  is the maximum radius of membrane pores,  $\theta$  is the contact angle membrane in liquid, and  $\gamma$  is the liquid surface tension. For cylindrical holes,  $B=1$ , and for irregular pores,  $0 < B < 1$ . The breakthrough pressure is the lowest pressure required on the liquid side in order for liquid to enter the membrane pores. The liquid surface tension, the hydrophobicity of the membrane, and the size and shape of the membrane pores are the three main components of anti-wetting membranes in a typical GLMC process. The performance of the membrane contactor, which in turn impacts the overall performance of the system, is determined by the properties of the membranes used. Commercially accessible hydrophobic polymeric membranes are mostly employed in nonwetted mode applications. Polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) are a few types of these membranes [12, 20, 23]. Interestingly, PTFE membrane has a higher wetting resistance than the

other membranes that were studied [20, 27, 28]. Significant considerations are given to the water contact angles of PVDF, PTFE, and PP membranes, which are around 100–127°, 92–130°, and 113–139°, respectively [4, 28, 29]. Even if the utilized membrane exhibits strong hydrophobicity (such as PP, PTFE, and PVDF), the absorbents, in particular alkanolamines (aqueous solutions of organic compounds), can permeate pores partially of the hydrophobic membrane, that is called partial wetting mode (Figure 2b) [30, 18, 31]. The gas–liquid interface is pushed to inside the membrane phase particularly in this case. A membrane morphology may alter as a result of partial wetting, which will reduce the membrane's hydrophobicity and affects its performance. As can be observed in the literature, certain studies have documented morphological alterations brought on by absorbent entering into membrane pores. The results of the systematic examination conducted by Barbe *et al.* [32] showed that the microporous PP membranes exhibited a general increase in porosity, pore length, and pore equivalent diameter following a 72-hour exposure to water. Immersion of alkanolamine solutions such as MEA and MDEA accentuates the increase in pore size [8]. Moreover, a decrease in contact angles generally denotes a decrease in surface hydrophobicity brought on by the absorbent-membrane interaction. In 30% MDEA for 60 days, there is a notable decrease in contact angles from 121.6° to 90.8° when PP membrane is used in this study. It is evident that both a decrease in the membrane's hydrophobicity and an increase in its pore size lead to wetting. Even a partial wetting of the membrane can cause a significant increase in membrane resistance because the liquid phase that results from the membrane wetting occupies the membrane pores [30, 33].

Research by Rangwala [33] indicates that even in situations where there are only 2% liquid-filled pores, the membrane resistance may account for as much as 60% of the overall mass transfer. This would ultimately lead to a large reduction in the acid gas transfer rate. The published work [34] shows that partial wetting of PP membrane pores by MEA absorbent considerably decreased the mass transfer rate of CO<sub>2</sub>. The mass transfer rate decreased to 59% of its starting value after 14 days of operation. Wetting occurs when the liquid absorbs into the membrane pores due to the transmembrane pressure, which is the pressure differential between the gas and the liquid, rising above the breakthrough pressure or critical transmembrane pressure. According to the Laplace–Young equation [35], the breakthrough pressure is determined by the pore size of the membrane, the surface tension of the absorption liquid, and the interaction between the membrane material and the absorption liquid (i.e. contact angle). Furthermore, a membrane with smaller pores may wet the membrane less. But in this instance, permeability will be reduced as a result in this case. Note that lowering the solution concentration may result in an increase in the surface tension of the absorption liquid, which could further affect selectivity. However, the use of superhydrophobic membranes can increase the contact angle, which is thought to be an effective method of preventing the desired absorption liquid from penetrating the pores.

### 3.0 SUPERHYDROPHOBIC MEMBRANE PREPARATION AND CHARACTERIZATION

Polymeric membranes are used as the phase separation barrier in the majority of membrane contactor processes.

There are various methods for fabricating porous membranes for membrane contactors, depending on the type of polymeric material used. Specific characteristics of microporous polymers are shown in Table 1 [120]. Although research on water-repellent or highly hydrophobic surfaces has been done for a long time, the phrase "superhydrophobic surface" is relatively new. According to published reports, a superhydrophobic surface characterization showed that its sliding

angle (SA), hysteresis contact angle (HCA), and water contact angle (WCA) were all below  $10^\circ$  and above  $150^\circ$ , respectively [36]. In order to obtain the high WCA, it is advised to use low surface energy material which include the role of surface morphology which supported this fact, but it is necessary to be combined superhydrophobic membranes, which are typically microporous in nature and are employed in membrane contactors.

**Table 1** Microporous polymers properties [120]

Membrane	Full name	Molecular mass <sup>a</sup> (g.mol <sup>-1</sup> )	Density <sup>a</sup> (g.cm <sup>-3</sup> )	Porosity <sup>a</sup>	Tortuosity <sup>b</sup>	Membrane pore size <sup>a</sup> (μm)	Surface energy <sup>c</sup> (dynes.cm <sup>-1</sup> )
PP	Polypropylene	42.08	0.85	0.32	8.82	0.2	30
PES	Polyether sulfone	232.26	1.37	0.40	6.40	0.2	46
PVDF	Polyvinylidene	64.03	2.00	0.38	6.9	0.2	25
PTFE	Polytetrafluoro-ethylene	100.02	2.30	0.36	7.47	0.2	19

<sup>a</sup> provided by the supplier; <sup>b</sup> measured from [121]; <sup>c</sup> taken from [122, 123]

### 3.1 Inorganic/ceramic Membranes

It is important to note that the polymeric membranes used in the contactors may be replaced by ceramic membranes. Because ceramic membranes are more resistant to heat and chemicals, they can be employed in environments with high temperatures and severe chemicals where most polymeric membranes would not function. Koonaphadeelert *et al.* [37] used the hydrophobically modified ceramic membranes for the first time to strip CO<sub>2</sub> from amine solutions. Researchers have focused more attention on mass transfer models, operating parameter impacts, module performance, and capacity. On the other hand, the high cost and challenge of producing flawlessly are the drawbacks of ceramic membranes. The most often

utilized inorganic materials (ceramics derived from metal oxides) for membrane preparation are silica, alumina, and zirconia. The hydroxyl (-OH) groups on the surfaces of these materials make them hydrophilic by nature. As a result, liquid water can pass through the membrane surface rapidly [38]. Therefore, ceramic membranes need to be surface modified to increase their hydrophobicity in order to be suitable for membrane contactors. Low surface energy materials are used to adopt surface modification by direct grafting utilizing fluoroalkyl silane (FAS) [38–39]. To speed up the grafting process, the ceramic membrane is usually immersed in FAS solution for a predetermined period of time. The Si–O–alkyl groups of the silane react with the OH groups on the ceramic

membrane surface during the grafting process [40]. Modified ceramic membranes with increased liquid entry pressure of water (LEP<sub>w</sub>) and WCA more than 150° have been successfully fabricated by researchers [39]. Using 10% sodium hydroxide (NaOH), Wongchitphimon *et al.* produced a highly hydrophobic PVDF-HFP membrane. They subsequently changed the membrane with a mixed solution of tetraethoxysilane (TEOS) and FS10, which led to an increase in contact angle of around 308 [41]. Nguyen *et al.* reported the composite membranes by coating a thin layer of hydrophobic polymers of PTMSP (poly(1-(trimethylsilyl)-1-propyne)) and Teflon AF2400 (fluoropolymers), respectively on the porous PP support [42]. In another recent work, Xue *et al.* [10] illustrated the detailed wetting process inside membrane pores using a unique membrane pore wetting model and the Laplace-Young equation. This was verified using numerical simulation of

molecular dynamics (MD). The suggested study investigated the wetting conditions of a ceramic membrane with a contact angle of 51.4° and an average pore size of 1.26 μm. The results demonstrated that the average or maximum pore diameters of the ceramic membrane could not be used to determine liquid and bubble breakthrough pressures with any degree of reliability. Furthermore, with ceramic membranes, the actual liquid and bubble breakthrough pressures were slightly lower than the critical pressures corresponding to the maximum pore size, or a hydrophilic ceramic membrane. The results for the hydrophilic ceramic membrane indicated that the membrane pore was in a wetting condition when the gas-liquid pressure differential was zero. The liquid pressure needs to be lower than the gas pressure in order to completely prevent membrane wetting. Table 2 displays research on the superhydrophobic ceramic membranes.

**Table 2** Superhydrophobic ceramic membranes prepared by FAS grafting method for membrane contactor

Ceramic Membrane	Grafting parameter	WCA (°)	LEP <sub>w</sub> (bar)	Process	Ref.
α-Al <sub>2</sub> O <sub>3</sub>		126.3		13 %CO <sub>2</sub> ; 30 wt% MEA CO <sub>2</sub> removal efficiency: 70% absorbent pressure is higher than gas pressure	145
α-Al <sub>2</sub> O <sub>3</sub>		120		20 % CO <sub>2</sub> ; Ultrapure water absorbent pressure is higher than gas pressure CO <sub>2</sub> flux (mol/m <sup>2</sup> .h): 28.08	146
Al <sub>2</sub> O <sub>3</sub>		124		15 %CO <sub>2</sub> ; 20 wt% MEA absorbent pressure is higher than gas pressure	147

Ceramic Membrane	Grafting parameter	WCA (°)	LEPw (bar)	Process	Ref.
				CO <sub>2</sub> removal efficiency: 91.8	
alumina tube with ZrO <sub>2</sub> layer	FAS: 2 wt.% grafting time: 24 h	153	6.5	CO <sub>2</sub> absorption using MEA	[39]
kaolin-alumina hollow fibre	FAS: 0.01 mol/L grafting time: 4 h	142	2.5	CO <sub>2</sub> absorption using water	[124]
γ-alumina membranes on α-alumina support	FAS: 0.1 mol/L eroding time*: 5 min grafting time: 24 h multiplicity: 4 times	164.5	-	-	[125]
Various ceramic materials for CO <sub>2</sub> absorption- Review article	-----	-----	-----	CO <sub>2</sub> absorption using various absorbtion liquis	[148]
Various ceramic materials for gas absorption- Review article	----	----	----	CO	[149]
Al <sub>2</sub> O <sub>3</sub> hollow fibre and use of 16 other ceramic membrane	-----	---	---	CO <sub>2</sub> absorption and MEAsolution as the liquid absorbent	[150]
Kaolin hollow fibre membranes prepared by the phase inversion process.	Various concentration of FAS	160°	-----	CO <sub>2</sub> absorption from natural gas and water as absorbent	[151]

### 3.2 HF Contactor with Polymeric Membranes

Unlike inorganic membranes, which can only be superhydrophobized

through surface modification, polymeric membranes can be superhydrophobized through direct processing or surface modification [43, 44]. Direct processing can be used to



achieve the superhydrophobic modification during the preparation process itself. The number of steps involved in surface modification could be one or more, depending on the material and technique selected.

### **3.2.1 Membrane Preparation Process-improvement**

Hydrophobicity can be enhanced in this direct processing method by improvement of phase separation process, blending method, or electrospinning. According to this technology, the surface morphology which is influenced by process and solution parameters is responsible for the intended increase in hydrophobicity. According to published reports, coagulants that delayed the demixing phase separation [45], long vapour exposure times that facilitated the crystallization process [46], and low air temperature and high PVDF contents facilitate the crystallization process, resulting in the formation of a porous skin and particle morphology, which increases the hydrophobicity of the surface [47]. A straightforward method for enhancing the hydrophobicity of a membrane is the blending method, which involves mixing low surface energy materials like surface modifying macromolecules (SMM) [48, 49, 50-53] or nanoparticles [54] into the casting solution. However, no published work is reported on superhydrophobic membrane preparation using these methods. Hybrid polyvinylidene fluoride-hexadecyltrimethoxysilane (PVDF-HDTMS) membranes were prepared in an interesting study using the non-solvent induced phase-inversion method. HDTMS acted as the hydrophobic modifier, and ammonia water was used as the dehydrofluorination reagent and non-solvent additive. A extremely hydrophobic hollow fiber membrane

for carbon dioxide (CO<sub>2</sub>) absorption using membrane contactor was the main objective of this study [55]. The membranes exhibited superhydrophobicity due to the formation of a rough nanoscale microstructure and low surface free energy of the outer surface. Images obtained using scanning electron microscopy showed that the rough microscale hierarchical spherulitic particles with a nanoscale stereoscopic coralliform microstructure made up the outer surfaces of the membranes. Scanning electron microscopy images revealed that the exterior surfaces of the membranes were composed of rough microscale hierarchical spherulitic particles with a nanoscale stereoscopic coralliform microstructure. There has been a great deal of study done on the electrospinning method for producing superhydrophobic membranes from polymer melts or solutions, with or without nanoparticles. Using a polystyrene (PS) solution, this approach has been used to make superhydrophobic membrane [56-57], PVDF [58], and PP [59]. It is interesting to note that superhydrophobic inorganic polymer composite membranes from PVD/SiO<sub>2</sub> have also been successfully prepared using this process [60-62]. Furthermore, this technique is employed to synthesize superhydrophobic polyurethane (PU)/terminal fluorinated polyurethane (FPU)/carbon nanotubes (CNTs) [63] and polyvinylidene fluoride-cohexafluoropropylene (PeH)/CNTs [64].

### **3.2.2 Methodology for Surface Modification of Desired Membrane**

A few surface modification techniques have been put forth in this area to produce a superhydrophobic membrane in a methodical manner. Among the crucial processes, chemical vapour

deposition (CVD), plasma treatment, and coating with hydrophobic polymer film that has been roughened are promising methods that can simultaneously make the membrane surface rough and hydrophobize it using low surface energy materials, resulting in superhydrophobicity. These techniques are also referred to as one-step surface modification. While the fluorine deposition provides the low surface energy, the etching technique used during the plasma treatment produced a rough surface on the membrane. Likewise, CF<sub>4</sub> [65–66], PTFE [67–68], and benzene [69] were effectively employed by several researchers to synthesize superhydrophobic polymer membranes using plasma treatment. Apart from the choice of plasma reagent, the working power and duration of plasma treatment are also critical aspects in this process. However, excessive treatment does not appear to improve superhydrophobicity, and in fact may even worsen it [65, 67, 70, 71]. For this reason, it is crucial to optimize both procedure parameters. Interestingly, coating with a roughened hydrophobic polymer film is also a suitable method for producing a superhydrophobic polymer membrane; this process can be carried out using non-solvent [29, 72–75] or nanoparticles [76]. There are published reports on the preparation of superhydrophobic polymer membranes using the CVD technique [77]. Apart from the one-step method, a two-step method of surface modification can also be employed to create a superhydrophobic membrane. This method involves roughening the surface first, then hydrophobization utilizing a low-surface-energy material, or the opposite. In this context, it is common practice to coat the membrane surface first with nanoparticles and then with fluorosilane chemicals. A number of researchers have successfully prepared

superhydrophobic membranes with surface roughening using TiO<sub>2</sub> [78], silver [79], and silica [80] nanoparticles under this process. In an effort to increase the HFMC-based PP membrane wetting resistance during the CO<sub>2</sub> capture process, Kim *et al.* [81] attempted to hydrophobize the PP membrane surface in a single step without the need for physical or chemical pretreatment by employing perfluoroether-grafted silane. The suggested fluorosilane (FS) was found to be appropriate for increasing the hydrophobicity of the PP membrane surface since it could be cured at a comparatively low temperature (298.15 K). Membrane characterization allowed for the confirmation of the FS coating layer on the PP membrane surface. Furthermore, the long-term stability and CO<sub>2</sub> absorption capacity of the FS-coated PP membrane were investigated in relation to gas flow rate variations. When compared better chemical stability and endurance of the selected membrane. The as-prepared FS-coated PP membrane may be used in gas-liquid membrane contactors for CO<sub>2</sub> capture from flue gas from coal-fired power plants, according to the authors. The synthesis of superhydrophobic membranes from polymeric materials and most recent developments in hydrophobic membrane modifications for gas absorption using membrane contactor systems are compiled in Table 3 [2]. It is important to note that, although membrane contactors have been applied for the absorption of acidic gases, including H<sub>2</sub>S and SO<sub>2</sub>, the hydrophobic membrane alterations used in these research have not been published [2]. As a result, Table 3 exclusively discusses the use of hydrophobically modified membranes for CO<sub>2</sub> adsorption. Using contacting membranes with and without hydrophobic changes, Goh *et al.* compared the CO<sub>2</sub> absorption

performance based on the data presented in Table 3. When compared to their non-modified equivalents, the hydrophobized membranes enhanced wetting resistance has always led to a larger CO<sub>2</sub> absorption flux [2].

### 3.3 Novel Liquid Absorbents and Recent Advancement

One of the several absorption liquids that the TNO group in the Netherlands has prepared and patented is CORAL (CO<sub>2</sub> removal absorbent liquid). This is based on the fact that certain combinations of amino acids and salts have a higher surface tension than others, which allows them to reduce the tendency of membrane wetting [82]. Similarly, ionic liquids have been studied for acid gas removal because of their strong affinity towards the same components. The primary rationale behind its adoption has been the benefit of simple CO<sub>2</sub> desorption from used ionic liquids following the physical absorption of CO<sub>2</sub> by ionic liquids [83].

The suitability of an ionic liquid, 1-ethyl-3-methylimidazolium ethylsulfate, for SO<sub>2</sub> removal in a gas-liquid membrane contactor was effectively established [84]. Moreover, it has been reported in published literature that the main drawback of ionic liquids for industrial use is their high viscosity, which can result in 97.8% of the total mass transfer resistance [85]. Further, increasing the mass transfer rate using the ionic liquid phase is crucial, necessitating an increase in the fluid dynamics of the system. Mass transfer studies using ionic liquid utilizing membrane contactors have been performed by a small number of researchers in parallel flow and transverse flow [86–87]. In a recently published study, Elmobarak *et al.* used supported ionic liquid membranes (SILM) to address several ionic liquid based difficulties while

performing experiments [87]. The assessment of SILMs performance was done dealing CO<sub>2</sub> capture technology which was the primary focus of authors. The basic configuration of SILMs is usually IL, which is attached by capillary forces to the pores of polymeric and/or inorganic membranes. The CO<sub>2</sub> carbon capture technology is considered as heterogeneous because SILM comprises of two phases and they consist of a solid phase membrane and a liquid phase connected to the ILs. To dissolve or diffuse ILs on membrane surfaces, several solute particles are used. Material loss was one of the main disadvantages of using traditional ILs in SILM, as stated in the literature. Gradually, in the improved version of SILM was unveiled, featuring a steady composition, reduced solvent loss, increased liquid phase stabilization, and a consistent performance with reduced evaporation. As a result, the benefits of ILs with unique properties including low volatility and excellent thermal and chemical stability were made possible by SILMs technology. Several studies have examined the application of SILMs technology for CO<sub>2</sub> uptake; the findings indicated that room-temperature-developed SILMs outperformed conventional polymers in CO<sub>2</sub> uptake from streams comprising CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>. In terms of CO<sub>2</sub> uptake, three ILs containing 1-n-hexyl-3-methylimidazolium ([hmim]) based on stable polysulfone asymmetric support ([PF6] or [PF4]) performed well. The combinations [hmim][BF4] and [hmim] [BF6] increased the absorption of CO<sub>2</sub> and separation factor to 26 from a mixture of CO<sub>2</sub> and CH<sub>4</sub>.

**Table 3** Recent advances made in hydrophobic membrane modification for gas absorption using membrane contactor system

Type of membrane	Strategy	Modification	Feed stream/flow rate	Absorbent/flow rate	Water contact angle absorption flux				Ref.
					Pristine	modified	pristine	Modified	
PVDF	Polymer dope additive	6 wt% SMM	CO <sub>2</sub> /100 ml·min <sup>-1</sup>	Distilled water/ 300 ml·min <sup>-1</sup>	84°	99°	0.72 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	5.4 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	131
PP			CO <sub>2</sub> /N <sub>2</sub> mixture composition(%) (15% vol. CO <sub>2</sub> ) 60 ml·min <sup>-1</sup>	IL 60				0.061 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	12
PVDF	Polymer dope additive	2 wt% SMM	CO <sub>2</sub> /100 ml·min <sup>-1</sup>	Distilled water/0.03 ml·s <sup>-1</sup>	86°	96°	–	0.7 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	54
PTFE			CO <sub>2</sub> /N <sub>2</sub> mixture composition(%) (15% CO <sub>2</sub> )	Aqueous MEA solution (30 wt%)				0.27 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	31
Alumina membrane			SO <sub>2</sub> conc. (ppm) 3300	[emim][EtSO <sub>4</sub> ] 1000 ml·min <sup>-1</sup>				0.005 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	84
Electrospun PS	Polymer dope additive	PMDS	2 wt% SMM	AMP-PZ/100 ml·min <sup>-1</sup>	greater than 128°	greater than 155	–	1.85 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	132
PEI	Nanofiller in MMM	1 wt% MMT	CO <sub>2</sub>	Distilled water/0.5 ml·s <sup>-1</sup>	77°	86°	–	1.09 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	133
PVDF	Nanofiller in MMM	5% ZSM5	CO <sub>2</sub>	Distilled water/1.2 ml·s <sup>-1</sup>	84°	104°	1.23 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	3.4 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	134
PVDF	Nanofiller in MMM	7 wt% graphene sheet	CO <sub>2</sub> /1.5 L·min <sup>-1</sup>	Distilled water/ 0.012 ml·s <sup>-1</sup>	87°	133°	–	3.0 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	135
PAN	Grafting	Tetrazole activation + decane grafting	CO <sub>2</sub> /1.5 L·min <sup>-1</sup>	Distilled water/240 ml·min <sup>-1</sup>	–	113°	0.54 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	1.9 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	136
PTFE	Coating	Silica	CO <sub>2</sub> + CH <sub>4</sub> /1000 ml·min <sup>-1</sup>	Potassium carbonate/75 ml·min <sup>-1</sup>	117°	158°	–	1.85 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	137
PVDF+PFTS	Coating	TiO <sub>2</sub>	CO <sub>2</sub>	MEA/0.25 ml·s <sup>-1</sup>	107°	120°	3.3 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	10.1 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	138
PVDF+PFTS	Coating	SiO <sub>2</sub> -TiO <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	MEA/0.25 ml·s <sup>-1</sup>	68°	124°	1.8 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	6.1 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	139
Alumina membrane	Coating	FAS aerogel	CO <sub>2</sub> + N <sub>2</sub> /20 ml·min <sup>-1</sup>	MEA/50 ml·min <sup>-1</sup>	-	-	–	6.0 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	140

Type of membrane	Strategy	Modification	Feed stream/flow rate	Absorbent/flow rate	Water contact angle    absorption flux				Ref.
					Pristine	modified	pristine	Modified	
Alumina membrane	Grafting/coating	FAS + PDMS/PVDF	CO <sub>2</sub> + N <sub>2</sub> /200 ml·min <sup>-1</sup>	MEA-PZ/50 ml·min <sup>-1</sup>	138°	150°	1.0 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	.5 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	141
Alumina membrane	coating	Silica aerogel	CO <sub>2</sub> + N <sub>2</sub> /2000 ml·min <sup>-1</sup>	MEA-PZ/50 ml·min <sup>-1</sup>	134°	150°	–	11.3 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	142
Alumina membrane	Grafting	APMTS- silica aerogel + FAS + tri-epoxy crosslinker	CO <sub>2</sub> + N <sub>2</sub> /2000 ml·min <sup>-1</sup>	MEA-PZ/50 ml·min <sup>-1</sup>	–	165°	– [	1.44 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	143
PVDF-HFP	Grafting	ZnO + FAS17	CO <sub>2</sub> + CH <sub>4</sub> /200 sccm	AMP-PZ/ 150 sccm	–	154°	–	2.10 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	143
PEI	Grafting/	Fluorinated silica	CO <sub>2</sub> /0.12 m·s <sup>-1</sup>	Distilled water/0.3 ml·s <sup>-1</sup>	109°	123°	-	2.65 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	144
PP or Al <sub>2</sub> O <sub>3</sub>			SO <sub>2</sub> removal Numerical 100–1000 ml·min <sup>-1</sup>	DMA				0.002 mmol·m <sup>-2</sup> ·s <sup>-1</sup>	152
PVDF/PDMS HF			NO <sub>x</sub>						153
PDMS HFMB			NO <sub>2</sub> , NO						154

The usage of polymeric membranes with ILs presents a great potential to fabricate SILMs with a greater selectivity and permeability than standard polymeric membranes, according to all of the previously published studies. Diffusion-controlled mass transfer is the basis for the gas transport mechanism [87]. Long-term compatibility of Ionic liquids with polymeric membranes, together with other drawbacks including high

investment costs and a lack of knowledge, have played a significant role in determining their commercial applications [85]. Ionic liquid technology is still in its infancy and has not yet found widespread use in large-scale applications. A few of the aqueous amine solvents for CO<sub>2</sub> loading and CO<sub>2</sub>/CH<sub>4</sub> selectivity employing membrane contactors were compiled in Table 4.

**Table 4** CO<sub>2</sub> loading and CO<sub>2</sub>/CH<sub>4</sub> selectivity of aqueous amines solvents [88]

Solvent	Conc.	CO <sub>2</sub> loading(mol CO <sub>2</sub> /mol amine)	Selectivity CO <sub>2</sub> /CH <sub>4</sub>
MEA (Monoethanolamine)	30 wt% <sup>a,f</sup> 2.5M <sup>b</sup>	0.058 <sup>a</sup> , 0.79 <sup>b</sup> 0.47 <sup>f</sup>	
DEA (Diethanolamine)	30 wt% <sup>f</sup>	0.50 <sup>f</sup>	
MDEA	50 wt% <sup>a</sup> 2.0 M <sup>d</sup>	0.52 <sup>a</sup> 0.97 <sup>d</sup>	
AMP a;	30 wt% <sup>a,f</sup>	0.80 <sup>a</sup> 0.63 <sup>f</sup>	
TEA (Triethanolamine)	30 wt% <sup>a,f</sup>	0.39 <sup>a</sup> ; 0.27 <sup>f</sup>	
2-Amino-1-butanol	2.5M <sup>b</sup>	1.34 <sup>b</sup>	
1-Amino-2-propanol	30 wt% <sup>a</sup> ; 0.5 M <sup>b</sup>	0.54 <sup>a</sup> ; 0.89 <sup>b</sup>	
4-Amino-1-butanol	30 wt% <sup>a</sup> 2.5 M <sup>b</sup>	0.59 <sup>a</sup> ; 0.89 <sup>b</sup>	
5-Amino-1-pentanol	2.5 M <sup>b</sup>	0.83 <sup>b</sup>	
Ethylamine	2.5 M <sup>b</sup>	0.69 <sup>b</sup>	
Propylamine	2.5 M <sup>b</sup>	0.97 <sup>b</sup>	
Butylamine b	2.5 M <sup>b</sup>	1.07 <sup>b</sup>	
Sec-butylamine	2.5 M <sup>b</sup>	0.85 <sup>b</sup>	
Isobutylamine	2.5 M <sup>b</sup>	0.73 <sup>b</sup>	
N-pentylamine	2.5 M <sup>b</sup>	0.90 <sup>b</sup>	
Hexylamine b	0.1 M <sup>b</sup>	2.36 <sup>b</sup>	
Ethylenediamine	2.5 M <sup>b</sup> 2.0 M <sup>c</sup>	1.28 <sup>b</sup>	180-800 <sup>c</sup>
1,3-Diaminopropane	2.5 M <sup>b</sup>	1.27 <sup>b</sup>	
1,2-Diaminopropane	2.5 M <sup>b</sup>	1.16 <sup>b</sup>	
1,4-Diaminobutane	2.5 M <sup>b</sup>	1.42 <sup>b</sup>	
Hexadimethylenediamine	2.5 M <sup>b</sup>	1.52 <sup>b</sup>	
1,7-Diaminoheptane	1.5 M <sup>b</sup>	1.35 <sup>b</sup>	
Diethylenetriamine	2.5 M <sup>b</sup> 2.0 M <sup>c</sup>	1.83 <sup>b</sup>	200–1000 <sup>c</sup>
Triethylenetetramine	2.5 M <sup>b</sup>	2.51 <sup>b</sup>	
Tetraethylenepentamine	0.5 M <sup>b</sup>	3.03 <sup>b</sup>	

Solvent	Conc.	CO <sub>2</sub> loading(mol CO <sub>2</sub> /mol amine)	Selectivity CO <sub>2</sub> /CH <sub>4</sub>
N-(2-Hydroxyethyl) ethylenediamine	2.5 M <sup>b</sup>	1.36 <sup>b</sup>	
N,N'-Bis(2-hydroxyethyl) Ethylenediamine	2.5 M <sup>b</sup>	1.21 <sup>b</sup>	
Piperidine <sup>b</sup>	0.5 M <sup>b</sup>	1.40 <sup>b</sup>	
2-Methylpiperidine	0.5 M <sup>b</sup>	1.14 <sup>b</sup>	
4-Aminopiperidine	0.5 M <sup>b</sup>	1.90 <sup>b</sup>	
Piperazine	0.5M <sup>b</sup>	1.30 <sup>b</sup>	
1-Methyl piperazine	0.5 M <sup>b</sup>	1.19 <sup>b</sup>	
trans-Piperazine, 2,5-dimethyl	0.5 M <sup>b</sup>	1.36 <sup>b</sup>	
N-ethylpiperazine	1.0 M <sup>b</sup>	1.43 <sup>b</sup>	
2-(1-Piperazinyl) ethylamine	1.0 M <sup>b</sup>	1.90 <sup>b</sup>	
2-(1-Piperazinyl) ethane	1.0 M <sup>b</sup>	0.90 <sup>b</sup>	
Azetidine	0.24 M <sup>b</sup>	2.43 <sup>b</sup>	
Diazabicyclo [2.2.2] octane	2.5 M <sup>b</sup>	0.83 <sup>b</sup>	
1,4- 4-(dimethylamino)-2-butanol	2.0 M <sup>d</sup>	0.98 <sup>d</sup>	
4-(dipropylamino)-2-butanol	2.0 M <sup>d</sup>	0.56 <sup>d</sup>	
4-(dibutylamino)-2-butanol	2.0 M <sup>d</sup>	0.35 <sup>d</sup>	
4-((2-hydroxyethyl)(methyl) amino)-2-butanol	2.0 M <sup>d</sup>	0.91 <sup>d</sup>	
4-((2-hydroxyethyl)(ethyl) amino)-2-butanol	2.0 M <sup>d</sup>	0.95 <sup>d</sup>	
Methyldiethanolamine	2.0 M <sup>d</sup>	0.83 <sup>d</sup>	
Amino acid salt	2.0 M <sup>e</sup>	0.32 <sup>e</sup>	

<sup>a</sup> Absorption at 313.15 K in 0.15 bar, ref. [126].

<sup>b</sup> Absorption at 30 °C in atmosphere pressure, ref. [127].

<sup>c</sup> Absorption at 295 K, ref. [128].

<sup>d</sup> Absorption at 298 K, ref. [129].

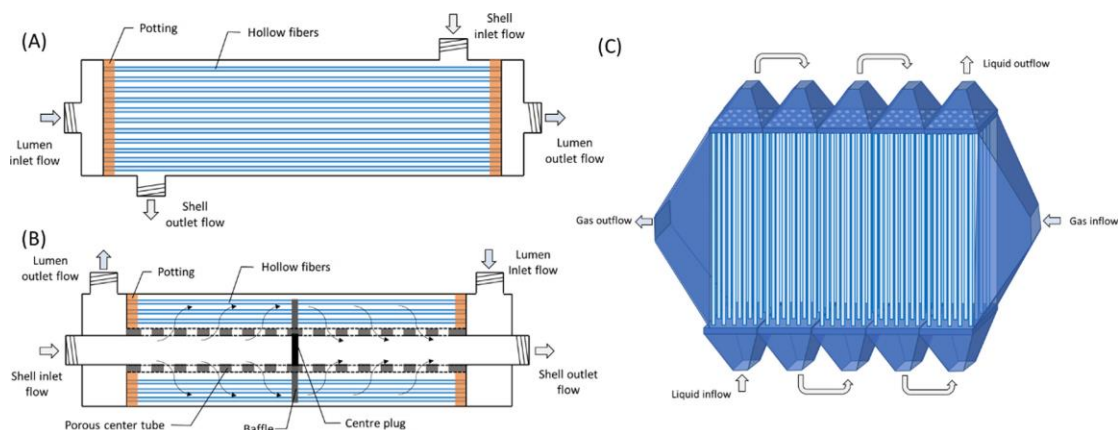
<sup>e</sup> Absorption at 295 K, ref. [82].

<sup>f</sup> Absorption at 313 K in 1.15 bar, ref. [130].

### 3.4 Recent Advances in Module Design and Process Simulation

Membrane contactors or hollow fiber membrane modules, are extensively employed in different configurations or modes. Two main types of hollow fiber membrane contactor modules have been widely employed for CO<sub>2</sub> absorption in GLMC processes: longitudinal flow, sometimes referred to as parallel flow, and cross-flow [88].

A schematic diagram of parallel-flow module is shown in Figure 3(A) [88]. The fluid and gas move parallel to each other on opposite sides of the hollow fibers, either concurrently or countercurrently [89, 90]. De-Montigny *et al.* [20] investigated counter-current and concurrent flow in a GLMC process and found that the former had a 20% higher mass transfer efficiency than the latter.



**Figure 3** Membrane modules showing (A) a parallel-flow and (B-C) two types of cross-flow hollow fiber MC modules (counter-current flow) [88]

Because the module is easy to assemble, the majority of lab-scale research have been conducted using longitudinal flow module design [91]. However, in comparison to the cross-flow module, the longitudinal flow module frequently offers a mediocre mass transfer efficiency. The fluid bypassing, channeling, and pressure drop on the shell side are the main causes of this [92]. Kim *et al.* [93] proposed an alternative method for CO<sub>2</sub> extraction by membrane gas absorption. This entailed incorporating into porous poly(vinylidene fluoride-cohexafluoropropylene) (PVDF-HFP) nanofibre membranes a two-dimensional zeolitic imidazolate framework (ZIF-L) with enhanced CO<sub>2</sub> adsorption capabilities. Using the electrospinning technique, composite structures of the nanofibre membranes with ZIF-L were fabricated. The adsorption of CO<sub>2</sub> molecules in ZIF-L cavities boosts CO<sub>2</sub> flux at moderate temperatures during both the absorption and stripping phases when utilized in composite nanofibre membranes. At 100°C, the PVDF-HFP membrane containing 5 weight percent ZIF-L thereafter exhibits 26.7 mmol m<sup>-2</sup> s<sup>-1</sup> of CO<sub>2</sub> stripping flux.

The Liquid-Cel® Extra-Flow module (CELGARD LLC, Charlotte,

NC, USA) is the most well-known cross-flow module made for GLMC. It has a central shell side baffle, and Figure 3(B) [88] shows the schematic diagram for it. By reducing bypass on the shell side and supplying a velocity component normal to the membrane surface, the baffle provides two primary benefits in terms of increasing mass transfer efficiency. When compared to parallel-flow modules, this results in a high-performance mass transfer [89]. The Kvaerner/Gore membrane modules, which are schematically shown in Figure 3(C) and have good mass-transfer characteristics and linear scale-up potential, are among the other complicated cross-flow modules that have already been fabricated and patented by K.A. Hoff [94]. To improve mass transfer, efforts are made to optimize the relative flow directions, packing density, and module structure, including fiber arrangement [95, 96]. The performance of various module designs on mass transfer were compiled by Mansourizadeh and Ismail [98] and Li and Chen [97]. The authors of these papers summarized a number of module designs, including coiled, crossflow, and longitudinal flow modules. Yang and Cussler [99] focused on building the parallel and crossflow modules and described about the processes dealing



with various aspects of regulating the mass transfer in each scenario in a important paper. From their trials, the researchers have deduced the mass transfer correlations, which they have tried to compare with the correlations previously published by other researchers for similar heat and mass transfer studies. The outcome these results provided a foundation for the fabrication of hollow fiber membrane modules.

Furthermore, Wickramasinghe *et al.* [100] have investigated the performance of crossflow and parallel flow modules using the equal flow per membrane area and equal flow per module volume. In both situations, it was found that crossflow modules outperformed parallel flow modules in terms of effectiveness. In contrast to the longitudinal flow module and crossflow module, the coiled hollow fiber module in both the tube and shell side may considerably boost mass transfer because of the secondary flows created inside the coiled fibers and the increased turbulence on the shell side [95, 101]. Boributh *et al.* [102] proposed a mathematical model for designing membrane module arrangement with optimum absorption performance in membrane contactor. A single-stage module, a two-stage module in parallel, a two-stage module in series with divided liquid flow, and a two-stage module in series with combined liquid flow were the four different membrane module designs that were examined for studied configuration. In next study, Boributh *et al.* investigated the design of multistage cascade membrane contacting process for chemical absorption of CO<sub>2</sub> [103]. These module designs offer helpful insights and guidelines for the scaling up of membrane contactors in real-world applications. Numerous mathematical models have been presented to replicate the process of gas

absorption in various membrane modules. Mavroudi *et al.* [104] examined the impact of process efficiency on operating conditions using modeling as a representative case. In the same direction, Wang *et al.* investigated pure CO<sub>2</sub> removal by absorption of three common alkanolamine solutions (AMP, DEA, and MDEA) in a hollow fiber membrane contactor using a theoretical simulation. On the other hand, the effects of different solvents, operating conditions and membrane characteristics were separately investigated by other researchers [105]. Ghobadi *et al.* [106] provided a 2D mass-transfer simulation model based on computational fluid dynamics (CFD) to separate CO<sub>2</sub> from a binary gas mixture of CO<sub>2</sub>/CH<sub>4</sub> using a PTFE hollow fiber membrane contactor. This investigation made it feasible to examine the effects of gas and liquid cross flow velocities on the overall performance of the membrane contacting system. The results demonstrated that while raising the liquid phase velocity improved the membrane system ability to absorb CO<sub>2</sub>, increasing the gas mixture velocity further resulted in deterioration in CO<sub>2</sub> separation. The effect of hollow fiber geometry on the removal of CO<sub>2</sub> is investigated and the results indicated that hollow fibers with smaller inner diameter provided higher effective mass-transfer area and therefore superior CO<sub>2</sub> removal performance. Additionally, computational fluid dynamics (CFD) techniques are also applied for the modeling of membrane contactors in recent years [107]. The state-of-the-art CFD methods applied on membrane processes and demonstrated the importance of CFD for understanding mass transfer in membrane processes was reviewed by Ghidossi *et al.* [108]. Using COMSOL software, a two-dimensional (2-D)

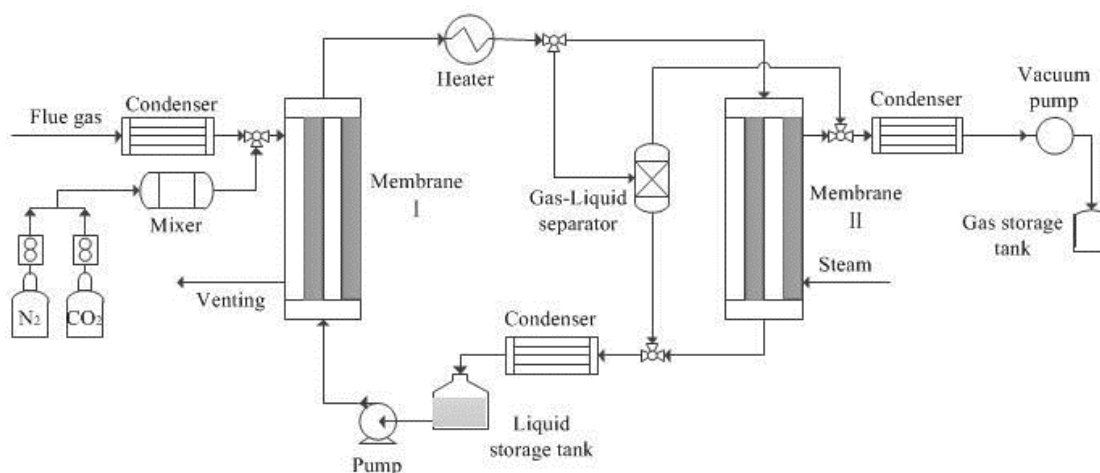
numerical module for simultaneous transport of gas stream  $\text{CO}_2/\text{H}_2\text{S}$  through hollow fiber membrane contactors using MEA was studied systematically [109].

#### 4.0 PERFORMANCE ANALYSIS OF SUPERHYDROPHOBIC MEMBRANE CONTACTOR

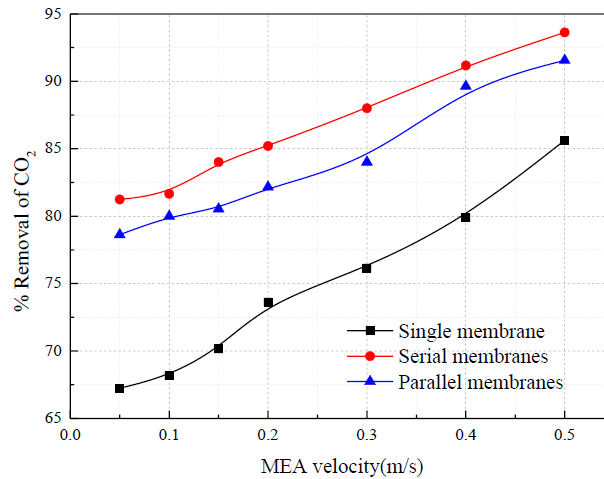
##### 4.1 Performances

In order to investigate on the absorption and desorption characteristics of membrane gas absorption and traditional separation methods, an experiment system of  $\text{CO}_2$  separation in a HFMC is proposed and depicted in Figure 4 [110]. This experimental process consists of the flue gas condensation, gas membrane absorption and  $\text{CO}_2$  desorption stage. Firstly, the coal-fired flue gas after cooling is sent into the membrane contactor, and then reacts with a counter currently with absorbent. The rich

solution is heated by a heater, and flows into the other membrane contactor or a gas-liquid separator. Absorbed  $\text{CO}_2$  will be released out of the solvent. Whereas the lean solution returns back to the liquid storage tank, and continues to flow into the whole system. Thus, high concentration of  $\text{CO}_2$  could be removed through the vacuum pump by controlling vacuum degree. Moreover, it is easy to take samplings from the input and output of the membrane contactor. Using the deionized water and  $0.5 \text{ mol l}^{-1}$  MEA as absorbents, Figure 5 [110] shows that when the MEA solution velocity is increased from  $0.05$  to  $0.5 \text{ m s}^{-1}$ , the  $\text{CO}_2$ -removal rate increased. This figure shows that serial membrane contactors have the highest  $\text{CO}_2$  absorption capacity. Since superhydrophobic modification has been shown to raise WCA and LEP, it may be inferred that, in contrast to hydrophobic membrane, superhydrophobic membrane is more resistant to wetting during real-world operation.



**Figure 4** A schematic diagram of hollow fiber membrane absorption of  $\text{CO}_2$  [110]



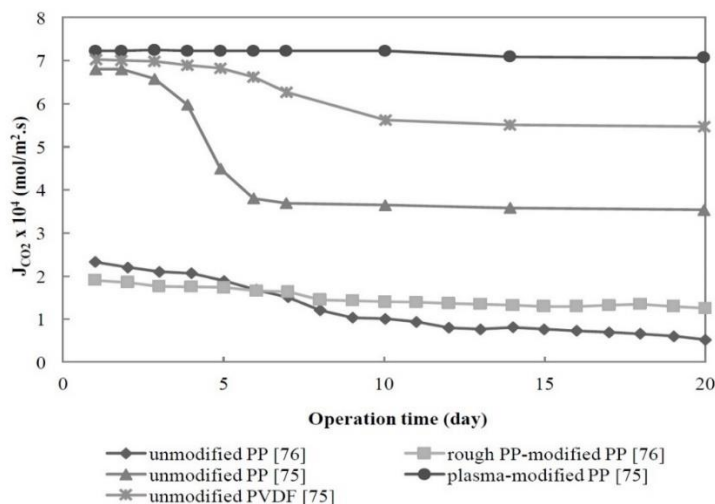
**Figure 5** Influence of MEA velocity on the CO<sub>2</sub> removal efficiency (feed compositions: CO<sub>2</sub>:N<sub>2</sub> = 14%:86%; gas pressure: 105 kPa; v<sub>g</sub>: 0.1 m s<sup>-1</sup>) [110]

Since the superhydrophobic membrane is not wetted, the gas–liquid contact at the pore mouth should be maintained, suggesting that the stationary liquid phase is not adding to the membrane resistance. Under these conditions, a high mass transfer rate of the acid gas can be attained. Table 3 [2] provides an overview of recent studies on the modification of hydrophobic membranes for gas absorption using membrane contactor devices. Published studies on membrane contactor utilized for acid gas removal indicated that either superhydrophobic ceramic membranes or superhydrophobic polymeric membranes exhibited a higher and more stabilised flux than commercial hydrophobic membrane [39, 68, 71, 72, 74]. Even after 30 days, the absorption flux of CO<sub>2</sub> using superhydrophobic PP membrane contactor decreased from  $7.4 \times 10^{-4}$  mol/(m<sup>2</sup> s) to  $7.1 \times 10^{-4}$  mol/(m<sup>2</sup> s) only, according to Lin *et al.* [71]. PP and hydrophobic PVDF membranes, on the other hand, had a considerable decrease in their CO<sub>2</sub> absorption flux; it passed from  $7.84 \times 10^{-4}$  mol/(m<sup>2</sup> s) to  $7.4 \times 10^{-4}$  mol/(m<sup>2</sup> s) and from  $7.05 \times 10^{-4}$  mol/(m<sup>2</sup> s) to  $5.52 \times 10^{-4}$  mol/(m<sup>2</sup> s), respectively. A high and steady

absorption flux can be produced by the decrease in wetting degree brought on by an increase in membrane hydrophobicity [67, 71]. Superhydrophobization of a polypropylene membrane can decrease the pore wetting degree by around 40% while increasing the membrane mass-transfer coefficient by over 207%, according to an analysis of important experiments. Nevertheless, studies revealed that the advantages of the membrane's porosity, pore size, and thickness are not outweighed by the superhydrophobic modifications and its negative effects on these parameters. Using a roughened polymer film coating method to prepare a superhydrophobic polymer membrane, Lv *et al.* [72] reported that within the first seven days, a slight reduction in CO<sub>2</sub> flux was seen, around 86% of the initial value. On the other hand, the CO<sub>2</sub> flux of the modified membrane was less than that of the unmodified membrane throughout the first six days, as illustrated in Figure 6. This is most likely the result of the modification process that increased membrane thickness and decreased surface porosity to achieve superhydrophobicity. As a result, it is

highly desirable to maximize the superhydrophobic modification technique while maintaining the critical

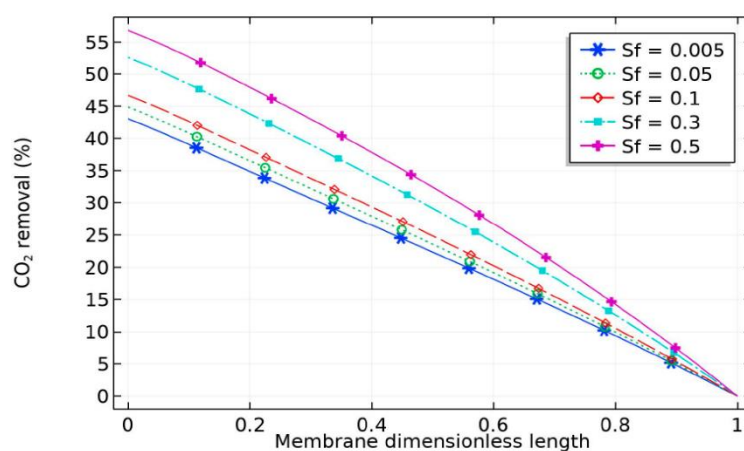
properties of membrane including thickness and porosity.



**Figure 6** Long-term performances of superhydrophobic membranes compared with hydrophobic membranes [119]

The effect of nanoparticle volume fraction is depicted in Figure 7 [111]. The diagram reveals that the percentage removal of CO<sub>2</sub> increased with solid nanoparticles, which can be attributed to the grazing effect (increase in the amount of CO<sub>2</sub> adsorbed into the surface of the CNT). Getting a homogenous solvent would reduce the rise, but at high CNT concentrations, this is not possible [111]. In a similar direction, Wu *et al.* produced superhydrophobic PVDF membranes

by using hydrophobic modified SiO<sub>2</sub> nanoparticles (HMSNs) [112]. The PVDF spherical microparticles that make up the synthesized superhydrophobic PVDF/HMSNs hybrid membrane were shown to be consistently skinless. Prewetted absorption flux of 2.34 mmol m<sup>2</sup> s<sup>-1</sup> was found at a fluid flow rate of 240 mL min<sup>-1</sup> and a mass ratio of HMSNs with PVDF matrix of 0.15:1, which was 3.3 times higher than the prewetted pristine PVDF membrane.

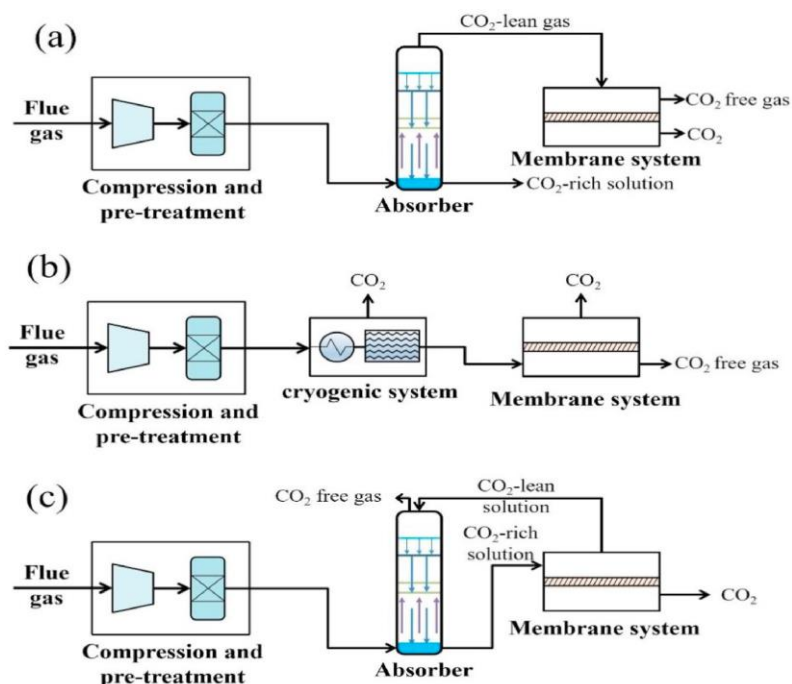


**Figure 7** Effect of CNT volume fraction on the percentage removal of CO<sub>2</sub>. Liquid and gas flow rates were both 10 mL/min. The solvent contained variable volume fraction of CNT, 5 wt % MDEA, with the balance being water. The feed gas contained 20 vol % CO<sub>2</sub>, with the balance being N<sub>2</sub> [111]

The authors concluded from these findings that hybrid membranes made of PVDF and HMSNs are excellent choices for CO<sub>2</sub> absorption applications. In another fascinating study, carbon dioxide (CO<sub>2</sub>) was separated from a gas stream using a polypropylene hollow fiber membrane contactor (PP HFMC) and the separation experiment was carried out under non-ultrasonic/ultrasonic irradiation for the first time. The nano adsorbents of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> were first synthesized and then dispersed in distilled water as a base fluid [113]. The results showed that Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanofluid, which benefited from a chemical reaction with CO<sub>2</sub>, was significantly more potent than Fe<sub>3</sub>O<sub>4</sub> nanofluid. Furthermore, the CO<sub>2</sub> absorption capabilities of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanofluids were successfully raised to 13.37 and 16.41%, respectively, by ultrasound irradiation. The CO<sub>2</sub> separation enhancement factors of 58.44 and 84.45% were obtained by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanofluid in both non-ultrasonic and ultrasonic irradiation settings.

In another study, silica nanoparticles (SiNPs) modified with hexamethyldisilazane (HMDS), dimethyldichlorosilane (DMDCS), and polydimethylsiloxane (PDMS) were used to generate mixed matrix membranes (MMMs) for carbon dioxide (CO<sub>2</sub>) absorption [114]. Out of the three SiNPs that were functionalized, the one that had HMDS treatment, known as TS-530, was evenly distributed throughout the PVDF polymer matrix. A membrane with a high porosity and a liquid entrance pressure of 77.57% and 7.51 bar, respectively, was the outcome of this. The authors recorded the

maximum selectivity of 22.5, more than three times larger than the clean membrane, and a CO<sub>2</sub> absorption flow of  $1.91 \times 10^{-4}$  mol/m<sup>2</sup>s. A different study was carried out dealing with dispersed CNT, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) at varied concentrations in aqueous monoethanolamine (MEA) solutions to prepare various amine-based nanofluids [115]. In order to remove CO<sub>2</sub> from nitrogen, the amine-based nanofluid was then employed as a liquid absorbent in a hydrophobic hollow fiber membrane contactor (HFMC). It is commonly recognized that the system may use larger liquid flow rates and transmembrane pressures when nanofluids are used. To investigate more about how NPs impact CO<sub>2</sub> removal and separation performance, the influence of effective parameters was assessed. According to the important findings of the study, employing nanofluids might reduce the need for adsorbent by 20% while also increasing CO<sub>2</sub> removal effectiveness by 5%. The effect of nanoparticle dispersion on mass transfer flow was examined using a unique enhancement factor ( $R_{\text{nano}}$ ). Numerical methods were used to find the ideal  $R_{\text{nano}}$  equation, enabling integration with general mass transport equations. The  $R_{\text{nano}}$  values discovered for the NPs used in this study ranged from 0.03 to 0.05. An interesting study [116] demonstrated membrane separation viability as a process hybridization option with existing CO<sub>2</sub> capture technologies. For CO<sub>2</sub> capture, three different hybrid process configurations using membrane technology were considered: in-series, parallel, and integrated. Figure 8 displays the in-series organization diagram.



**Figure 8** Schematic diagram of the in-series arrangement: (a) the absorption-membrane system, (b) the cryogenic-membrane system and (c) the absorption-membrane system with membrane desorption [116]

There are three types of membrane systems: (a) absorption, (b) cryogenic, and (c) absorption with membrane desorption. When compared to other conventional techniques, the hybrid systems have demonstrated reduced energy consumption for CO<sub>2</sub> capture. Moreover, the amalgamation of several CO<sub>2</sub> capture techniques and the multiple arrangements of these procedures (such as parallel, integrated, and in-series) facilitated increased adaptability in process design and the management of an extensive array of input gas circumstances. Engineers and researchers will be able to process hybridize the CO<sub>2</sub> capture process to optimize and change it with the help of this capability. Identifying the decisive factor is challenging since hybrid processes are more complex. In the end, this affects how well the process captures CO<sub>2</sub>. Compared to in-series or parallel hybrid systems, the CO<sub>2</sub> removal method based on membrane contactors offers a more integrated process scheme. This offers a large

contact area per unit volume, requires relatively little energy, and has a low investment cost. According to the authors, membrane contactors demonstrate positive economic efficiency and overcome the drawbacks of the hybrid processes mentioned above in terms of process complexity.

#### 4.2 Efficient Cleaning of Hollow Fiber Membrane

Fouling is a significant technical problem in pressure-driven membrane processes, including microfiltration and ultrafiltration, involving porous membranes. However, since there is no convective flow through the membrane pores in a membrane contactor, fouling is not as significant as observed in a membrane filtration system. Furthermore, because of the narrow membrane contactor diameter in industrial applications like coal-fired power plants, gas and liquid streams containing suspended particles can block the pores. Remarkably, a number

of investigations have demonstrated the ability of superhydrophobic surfaces to self-clean [117]. A different study looked at how the hydrophobic properties of the polyvinylidene fluoride (PVDF) membrane were affected by the addition of nano-graphite and poly(vinyl chloride) (PVC). Using the non-solvent induced phase separation approach, novel physical blending modified membranes were developed [118]. The PVDF-PVC/nano-graphite combination created in the experiment increases the hydrophobic characteristics of the PVDF membrane and decreases the cost of the composite membrane by adding PVC. PVDF membranes have more applications because of their durable self-cleaning ability. In order to lessen membrane fouling, it has been proposed that superhydrophobic membranes be utilized in membrane contactors. There aren't many public reports available on this instance. Yu *et al.* [39] proposed in a different study that ceramic membranes possessing superhydrophobicity had superior anti-fouling capabilities in comparison to PP membranes lacking this property. In contrast, carbon powder on the surface of the hydrophilic and hydrophobic ceramic membranes could not be successfully removed, but carbon powder on the superhydrophobic ceramic membrane could be cleaned with ease. Additionally, after a month-long operation utilizing flue gas from thermal power plants, there was no dust on the surface of the superhydrophobic ceramic membrane. On the other hand, the flue gas particles clogged the PP membranes.

## 5.0 CONCLUSION AND FUTURE DIRECTIONS

The membrane contactor technology is methodology that has gained significant

attention for the removal of acid gas due to its advantages over conventional methods. To achieve the necessary performance and stability for a realistic long-term operation, there remain some persistent challenges that require innovative solutions. On the other hand, membrane wetting caused by liquid absorbent turns into a minor issue that impairs membrane function. Superhydrophobic membrane contactors were subsequently developed as a solution to this issue, either from polymer or inorganic materials. It is possible to fabricate superhydrophobic polymer membranes by using either direct processing or surface modification techniques. Researchers also investigated the preparation of superhydrophobic membrane contactors for the removal of acid gases by supporting surface modification of hydrophobic polymer membranes by plasma treatment, nanoparticles or solvent/non-solvent coating technique. The hydrophilic characteristic of inorganic membranes necessitates surface modification in order to confer superhydrophobicity. As showed from the published data that a greater and more stable flow was obtained with an increase in hydrophobicity as compared to the unmodified membrane. However, a number of variables that affect the merits of superhydrophobicity must be taken into consideration, including extra membrane thickness and pore obstruction brought on by surface modification. Superhydrophobic modification not only provides a wetting-resistant membrane but also enables self-cleaning properties. Many research works in this important area indicate that using membrane contactors in industrial flue gas streams opens up new possibilities. In order to prepare a superhydrophobic microporous membrane that will improve membrane contactors in the

future, the main considerations are porosity, thickness addition, decrease in pore size, and stability of superhydrophobicity. The flue gas from the combustion process is hot, therefore it is also important to investigate the thermal and chemical stability of superhydrophobic membrane and synthesize specific absorbents for this usage. The fouling mechanisms that have been identified so far pertain to both osmotically-driven and membrane distillation processes, which are distinctly different from membrane contactor processes due to their separate driving forces. Therefore, it is essential to understand how the membranes utilized in MC goes under fouling. Additionally, more research is needed to determine the impact of novel membrane designs such as MMMs, composite, Janus, and omniphobic membranes particularly with regard to membrane fouling. Above all, there is even more need to optimize the process design for these new GLMC membranes due to the advancements in polymer-based membranes. Energy and techno-economic analyses should be part of these efforts to determine the real advantages and potential that these high-performance membranes can offer in terms of long-term operational basis. On the other hand, the design of high-efficient membrane modules must progress alongside the development of advanced membranes for GLMC processes. In this regard, when designing the geometry of the membrane modules for GLMC application, the goal should be to minimize the mass transfer resistance from the liquid phase, particularly for the physical absorption and stripping applications

#### CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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