



## Review

## Hollow fiber gas–liquid membrane contactors for acid gas capture: A review

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## ABSTRACT

Membrane contactors using microporous membranes for acid gas removal have been extensively reviewed and discussed. The microporous membrane acts as a fixed interface between the gas and the liquid phase without dispersing one phase into another that offers a flexible modular and energy efficient device. The gas absorption process can offer a high selectivity and a high driving force for transport even at low concentrations. Using hollow fiber gas–liquid membrane contactors is a promising alternative to conventional gas absorption systems for acid gas capture from gas streams. Important aspects of membrane contactor as an efficient energy device for acid gas removal including liquid absorbents, membrane characteristics, combination of membrane and absorbent, mass transfer, membrane modules, model development, advantages and disadvantages were critically discussed. In addition, current status and future potential in research and development of gas–liquid membrane contactors for acid gas removal were also briefly discussed.

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## Nomenclature

$A$	gas/liquid contact area ( $m^2$ )
$C$	concentration ( $mol/m^3$ )
$d$	diameter (m)
$D$	diffusion coefficient ( $m^2/s$ )
$E$	enhancement factor
$E_{\infty}^*$	modified infinite enhancement factor
$Gz$	Gratez number
$H$	Henry's law constant
$Ha$	Hatta number
$Ha^*$	modified Hatta number
$J$	absorption flux ( $kmol/m^2 s$ )
$k$	mass transfer coefficient (m/s)
$K$	overall mass transfer coefficient based on inner surface of the hollow fiber (m/s)
$l$	thickness (m)
$L$	fiber length (m)
$m$	distribution coefficient
$M$	molecular weight
$P$	pressure (Pa)
$Q$	flow rate ( $m^3/s$ )
$r$	radius (m)
$R$	gas constant, reaction rate ( $mol/m^3 s$ )
$Re$	Reynolds number
$Sc$	Schmidt number
$Sh$	Sherwood number
$\overline{Sh}$	average Sherwood number
$t$	time (s)
$T$	temperature (K)
$u$	flow velocity (m/s)
$\bar{u}$	average flow velocity (m/s)
$x$	pore length wetted by liquid (m)
$x^*$	wetting ratio

### Subscript

$A$	component A
$B$	component B
$e$	free surface
$g$	gas
$h$	hydraulic
$i$	inside, at the interface, i component
$Kn$	Knudsen
$l$	liquid
$Lm$	log mean
$m$	membrane, molecular, partial reaction order
$n$	number of fibers, partial reaction order
$o$	outside
$p$	pore
$s$	inner module

### Greek letters

$\alpha$	constant
$\gamma$	surface tension (dynes/cm)
$\varepsilon$	porosity
$\theta$	contact angle
$\mu$	dynamic viscosity (Pa s)
$\tau$	tortuosity
$\nu$	stoichiometric coefficient
$\varphi$	packing density
$\Omega$	dimensionless function of temperature

## 1. Introduction

It is important to devise techniques which would reduce acid gases like  $CO_2$ ,  $H_2S$  and other sulphuric components arising from the combustion of fossil fuels, present in natural gas, industrial gas and domestic processes effluent gas. They may have to be removed from the gas streams for environmental, economical and operational reasons. Therefore, efficient and flexible technologies capable to remove acid gases are needed operating over a wide range of concentration levels and a wide range of flow rates.

Conventional industrial methods to reduce acid gases employ gas absorption devices like packed towers, spray towers, venture scrubbers, bubble column etc. In these devices gas–liquid contacting is achieved by dispersing the gas phase in the liquid phase to obtain large contact areas thereby increasing the mass transfer rate. Even though these contacting methods are very popular in industry they have several drawbacks such as difficulty of obtaining an accurate estimate of the gas–liquid mass transfer area and a limited range of gas and liquid flow rates due to operational problems.

Polymeric membranes which are usually nonporous have been used for separation of gases. Commercial utilization of separation of gases through solid membranes is still somewhat limited due to low permeability and low separation factors. To overcome these problems membranes are being developed which are thinner, more selective and can withstand high temperatures.

In recent years, an alternative technology that overcomes the disadvantages of conventional gas absorption approaches and membrane gas separation is non-dispersive gas–liquid contact via a microporous membrane. By using a suitable membrane configuration such as a hollow fiber, fluids can be contacted on opposite sides of the membrane and the gas–liquid interface is formed at the mouth of each membrane pore. Mass transfer occurs by diffusion across the interface just as in traditional contacting equipment. Furthermore, in contrast with more conventional applications such as microfiltration, ultrafiltration and reverse osmosis, the driving force for separation is a concentration rather than a pressure gradient; indeed only a very small pressure drop across the membrane is required to ensure that the gas–liquid interface remains immobilized at the mouth of the pore.

These gas–liquid membrane contactors offer several advantages over conventional contacting devices such as high surface area per unit contactor volume, independent control of gas and liquid flow rates without any flooding, loading, weeping, foaming or entrainment problems, small size, known gas–liquid interfacial area, modular and being easy to scale up or down. So these advantages paved the way for the application of membrane contacting technology in the removal of acid gases from flue gases, natural gas and various industrial process gas streams that have led a number of investigators to explore a number of applications. Esato and Eiseman [1] were the first to employ the microporous membrane as a gas–liquid contacting device using hydrophobic flat Gore-Tex membranes of polytetrafluoroethylene (PTFE) for oxygenation of blood. Removal of  $CO_2$ , one of the major greenhouse gases, from gas streams by a membrane contactor has been a research focus since 1980s and for this purpose investigators have considered several factors like absorption solutions, membrane materials, membrane modules etc. to improve performance of  $CO_2$  removal [2–31]. Qi and Cussler [32,33] were the first to develop the idea of the hollow fiber membrane contactor for  $CO_2$  absorption using a microporous non-wetted polypropylene membrane where aqueous sodium hydroxide solution was used as an absorbent. Feron and Jensen [17] employed porous polyolefin membranes with the novel absorption liquids (CORAL) for removal of carbon dioxide from various feed gases. Ren et al. [34] prepared poly vinylidene fluoride (PVDF) hollow fiber membranes to make membrane contactors for  $CO_2$  capture. The hollow fiber membranes were spun with two

different dope solutions at different shear rates in order to understand the influences of the rheological characteristics of the dope solution on the membrane structure and the system performance for CO<sub>2</sub> absorption.

Although most of the researches are focused on the carbon dioxide removal, some others were conducted on removal of the other acid gases [35–42]. Lee et al. [35] obtained SO<sub>2</sub> removal efficiencies and mass transfer coefficients in the hollow fiber membrane contactors at various gas and liquid flow rates. Recently, some researches have been done on the removal of H<sub>2</sub>S from gas streams by membrane contactors [38–41]. Applications, advantages and disadvantages of hollow fiber membrane contactors have been discussed in more detail by Gabelman and Hwang [43]. Li and Chen [44] have reviewed absorption of CO<sub>2</sub> using chemical solvents in hollow fiber membrane contactors.

In the present paper, the important aspects of acid gas removal by hollow fiber gas–liquid membrane contactors such as liquid absorbents, membrane characteristic, membrane-absorbent combination, hollow fiber membrane modules, mass transfer and model development have been reviewed. Furthermore, advantages and disadvantages of the technology, current status and future directions of gas–liquid membrane contactors for acid gas capture were critically discussed.

## 2. Liquid absorbents in membrane contactors

A separation process using absorption involves transfer of one or more species from the gas phase to the liquid phase. In general, the absorption process can be categorized as a physical absorption or a chemical absorption. In the case of physical absorption the gas component is physically dissolved in the liquid phase, while in the case of chemical absorption the gas component reacts chemically in the liquid phase. To design an absorber system using either physical or chemical absorption, detailed information is required on the diffusivities and the solubilities of gas components in the liquid bulk as well as on the reaction rate kinetics.

Ideally, in the gas absorption process pores of the membrane should be completely gas-filled, to minimize any mass transfer resistance due to the presence of the membrane. Therefore, the membrane itself usually doesn't offer any selectivity for the gases to be separated; this role is fulfilled by the liquid absorbents. Reactive liquid absorbents are preferred to physical liquid absorbents as their absorption rate and capacity are generally much better. This feature not only results in a reduction in the size of the contactor, but also the solvent circulation rate. Various liquid absorbents have been considered to be applied for acid gases removal in membrane contactors. The absorbents include pure water, aqueous solutions of NaOH, KOH, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub>, NaHCO<sub>3</sub>, NH<sub>3</sub>, amines (MEA, DEA, MDEA, TEA, AMP, DGA, DIPA) and amino acid salts.

Selection of liquid absorbents should be based on some criteria. Using high reactive solution for the gas component can lead to higher absorption rate and reduction of liquid mass transfer resistance. Lu et al. [45] used 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ) as activators which were added into methyldiethanolamine (MDEA) solution, respectively, to form two aqueous solutions of activated MDEA for CO<sub>2</sub> capture from CO<sub>2</sub>/N<sub>2</sub> mixture. Korikov and Sirkar [46] also studied gas permeance of carbon dioxide from a CO<sub>2</sub>/N<sub>2</sub> mixture having a low CO<sub>2</sub> concentration into highly reactive absorbent like aqueous KOH solution through flat microporous PTMSP membrane.

One of the most important factors for absorbent selection is the surface tension of liquid absorbent. Although, the membrane used for gas absorption is generally hydrophobic microporous, absorbent solutions with low surface tension can penetrate inside the membrane pores and cause the membrane wetting gradually with time.

Generally, organic components can reduce the surface tension of absorbent solution and unfortunately the most of conventional absorbents, amine solutions, have an organic base. Therefore, researchers have been trying to develop the best absorbent for gas absorption in membrane contactors. Yan et al. [29] studied a new absorption liquid based on the amino acid salt in the experimental PP (polypropylene) hollow fiber membrane contactors. They used a new liquid absorbent, aqueous potassium glycinate (PG), with high surface tension to avoid the wetting problem of commercial PP microporous membrane. Their results showed that the solution has good reactivity towards CO<sub>2</sub> compared with the conventional absorbents like MEA and MDEA.

Liquid absorbents must have a good chemical compatibility with the membrane materials. It is an important factor that decides the long-term stability of the membrane module. Although, the most absorbents with a high acid gas loading capacity are highly corrosive the polymeric membranes in the membrane contactors have to be in direct contact with the absorbent. It was observed that two polypropylene membranes, Celgard 2500 and Accurel 1E-PP, underwent changes in surface morphology after being exposed to water for 72 h [47]. In another research, Wang et al. [24] studied the effects of DEA absorbent on the surface properties of PP microporous hollow fiber membranes in terms of morphology and surface tension by means of SEM, AFM as well as a contact angle Goniometer. It was found that hollow fiber PP membranes suffered changes in terms of pore structure and surface roughness after being exposed to DEA aqueous solutions.

Easiness of regeneration is another factor for absorbent selection. This factor is important in the processes where the absorbent solution must be recycled. Aqueous solution of amines are preferred for this purpose since they are generally considered weak bases that will react with acidic gases to form complexes with weak chemical bonds. These chemical bonds are easily broken by heating and reducing pressure, thus leading to absorbent regeneration. Yeon et al. [25] applied a pilot membrane contactor hybrid process to recover CO<sub>2</sub> from the flue gas. They used a porous PVDF hollow fiber module and its performance was compared with a conventional packed column. They also applied a thermal stripping tower with steam to regenerate absorbent solution, monoethanolamine (MEA) and triethanolamine (TEA), and recycled it to the process.

## 3. Membrane characteristics

In the last decades gas–liquid membrane contactors equipped with microporous hydrophobic membranes were widely tested for separation processes especially gas absorption to replace conventional equipment. As shown in Table 1, the hollow fiber membrane contactor can offer a much larger contact area per unit volume than other conventional absorbers. Therefore, the membrane contactors can become more efficient for gas absorption than conventional equipment [50] and may reduce the size of gas absorber and stripper units by 63–65% [25]. This effectiveness is possible by using a membrane with highly porous structure. However, the gas absorption application in membrane contactor requires a high level of safety in prevention of absorbent penetration into the membrane, especially in severe operation situation.

**Table 1**  
Specific surface area of some contactors.

Contactor	Specific surface area (m <sup>2</sup> /m <sup>3</sup> )	Reference
Free dispersion column	1–10	[48]
Packed column	100–800	[49]
Mechanically agitated column	50–150	[48]
Membrane contactor	1500–3000	[18]

**Table 2**  
Characteristics of hollow fiber membranes used in gas absorption contactors.

Membrane	ID ( $\mu\text{m}$ )	OD ( $\mu\text{m}$ )	Pore Size ( $\mu\text{m}$ )	Porosity%	Process	Reference
Polysulfone(PS)	200	400	0.05	–	SO <sub>2</sub> absorption with NaOH, Na <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> SO <sub>3</sub> and NaHCO <sub>3</sub> solutions	[34]
Polysulfone(PS)	560	880	0.102	–	H <sub>2</sub> S absorption with NaOH solution	[13]
Polyethersulfone(PES)	460	850	–	–	H <sub>2</sub> S absorption with NaOH solution	[13]
Polyethylene(PE)	482	706	–	0.82	CO <sub>2</sub> absorption with MEA solution	[5]
Polytetrafluoroethylene (PTFE)	1000	1700	–	0.40	CO <sub>2</sub> absorption with MEA solution	[5]
PP	600	1000	0.265	0.79	CO <sub>2</sub> absorption with CORAL 20 solution	[17]
PP	270	300	0.015	0.30	CO <sub>2</sub> absorption with water, DEA and NaOH solutions	[9]
PP	344	442	0.02–0.2	>0.45	CO <sub>2</sub> absorption with PG, MEA and MDEA solutions	[30]
Poly(vinylidene fluoride) (PVDF)	300	514	–	0.698	CO <sub>2</sub> absorption with pure water	[51]
PVDF	607	907	0.04	–	H <sub>2</sub> S and CO <sub>2</sub> absorption with Na <sub>2</sub> CO <sub>3</sub> solution	[40,41]
PP	244	300	–	0.35	CO <sub>2</sub> absorption with MEA and AMP	[53]
PTFE	1000	2000	–	0.50	CO <sub>2</sub> absorption with MEA and AMP	[53]

Principally different types of membrane such as symmetric hydrophobic porous membranes or asymmetric membranes with ultra-thin layer can be used as a gas–liquid membrane contactor [51,52]. In both case the membrane must be able to separate the contacting fluids. Typical membranes applied are prepared from hydrophobic polymer materials possessing a high porosity, a membrane thickness of 10–300  $\mu\text{m}$  and providing microfiltration properties with pore size of 0.1–1  $\mu\text{m}$ . Table 2, shows the characteristics of hollow fiber membranes used in the gas absorption membrane contactors.

### 3.1. Membrane materials

The choice of membrane material affects phenomena such as absorption and chemical stability under condition of actual application. This implies that the requirements for the polymeric material are not primarily determined by the permeability and hydrophobicity but also by the chemical and thermal properties of the material.

Among various hydrophobic polymers, polypropylene (PP), polyethylene(PE) and polytetrafluoroethylene (PTFE) are the most popular membrane materials. However since PE, PP and PTFE cannot be dissolved in solvents then the membranes are usually provided by stretching and thermal methods. Therefore, relatively low porosity resulting membranes restrict a significant increase on absorption flux. Consequently the main advantage of the microporous hollow fiber membrane i.e. a high area to volume ratio cannot be fully obtained. However, one of the significant properties of PTFE membrane is that it has a high resistance to wetting after several hours of operation. A study by Falk-Pederson and Dannstorm [12] suggested that PTFE is the only suitable membrane for use with alkanolamines.

PVDF membranes have excellent chemical and thermal resistances which make it stable in most of the corrosive chemicals and organic compounds such as acids, alkaline, oxidant and halogens [54]. However, PVDF membrane is conditionally suitable for alkaline solutions. It can be attacked by medium concentration alkaline solutions. In addition, since PVDF material can be dissolved in organic solvents used to prepare asymmetric membranes via phase-inversion method [55–58]. Therefore, the preparation of PVDF and modified PVDF membranes has been an active subject for various membrane based separation applications including membrane distillation, pervaporation and gas absorption [38–42].

An inorganic membrane could be used as an alternative barrier which provides better chemical and thermal stability as well as high mechanical strength. Ceramic membrane is another option for gas absorption membrane contactors. However, most of ceramic materials are hydrophilic in nature, because of the presence of its hydroxyl (–OH) group. This characteristic is considered to be a disadvantage as the wetted membrane has much higher membrane resistance than that of non-wetted membrane.

Thus membrane surface modification is required to improve its hydrophobicity. Koonaphapdeelert and Li [59] prepared ceramic hollow fiber membranes from aluminum oxides (Al<sub>2</sub>O<sub>3</sub>) using a phase inversion-sintering method. Membranes with different porosities and microstructure were produced by varying the alumina powder/polymer ratio in the spinning suspension and sintering temperatures.

### 3.2. Membrane properties

So far, most of the researches on the gas–liquid membrane contactors are at the stage of laboratorial and the long-term stability of the membrane has seldom been considered in the literature. Fouling is one of the major problems in the application of porous membranes. Fortunately, in the gas–liquid contactor applications, the contactors are less sensitive to fouling since there is no convection flow through the membrane pores. However, in industrial applications, gas and liquid streams with large content of suspended particles can cause plugging due to the small hollow fiber diameter. Pre-filtration is necessary in such a case.

The chemical stability of the membrane material has a significant effect on its long-term stability. Any reaction between the solvent and membrane material could possibly affect the membrane matrix and surface structure. Liquid absorbents with high load of acid gases are corrosive in the nature, which make the membrane material less resistance to chemical attack. Barbe et al. [47] examined surface morphology changes of hydrophobic Celgard 2500 and Accurel 1E-PP membranes during initial contact with water using scanning electron microscopy (SEM) and image analysis. The surfaces of both membranes showed increases in several of the following morphology parameters after 72 h of contact: porosity, pore area, pore length, pore breadth, pore equivalent diameter and pore spread factor. This was attributed to non-wetting intrusion of the water meniscus into some pores with a resulting enlargement of pore entrances. To ensure the long-term stability and the maintenance of the gas removal efficiency, the compatibility of the membrane to the liquid absorbent needs to be investigated.

The thermal stability of the membrane is another important parameter in the case of gas absorption. Under high temperatures, the membrane material may not be able to resist to degradation or decomposition. Changing in the nature of membrane depends on the glass transition temperature  $T_g$  for amorphous polymers or the melting point  $T_m$  for crystalline polymers. Over these temperatures, the properties of the polymers change dramatically. The glass transition temperatures for the commonly used polymers, in gas absorption membrane contactors, are shown in Table 3. It indicates that PE and PP have very low  $T_g$  values. This could contribute to the reported instability and wetting problems associated with them. The transition temperature of a polymer is determined largely by its chemical structure, which includes mainly the chain flexibility

**Table 3**  
Glass transition temperature  $T_g$  of polymers [60].

Polymer	$T_g$ (°C)
Polytetrafluoroethylene	126
Polypropylene	-15
Polyethylene	-120
Polyether sulfone	230
Polysulfone	190
Polyvinylidene fluoride	-40
Polyimide(Kapton)	300

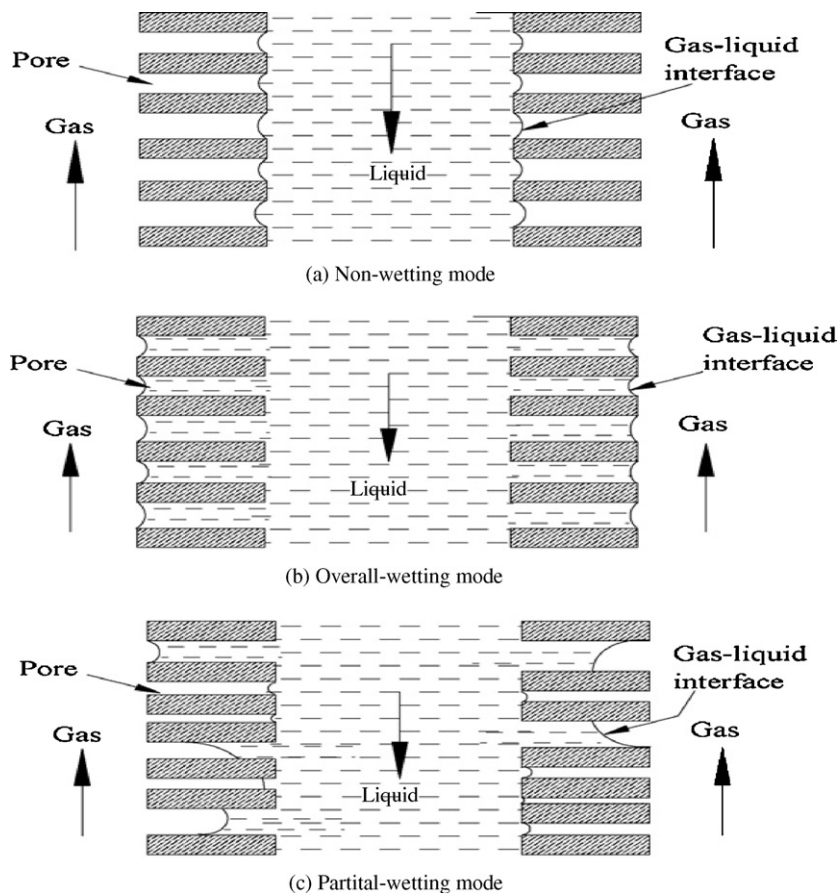
and chain interaction. PTFE, which has four fluoride side groups on the flexible polyvinyl chain, has a less flexibility and a much higher  $T_g$  compared to polyethylene and polypropylene. This feature contributes to its higher stability. In general, the factors that increase the  $T_g/T_m$  or the crystallinity of a membrane can enhance both its chemical and thermal stability. Therefore, in terms of long-term stability membrane material with suitable  $T_g$  needs to be applied. For  $H_2S$  removal from natural gas, membrane with moderate  $T_g$  can be considered since the separation can be carried out at ambient temperatures. However, for the  $CO_2$  absorption from flue gases, membrane with high  $T_g$  (possibly over  $100^\circ C$ ) may need to be applied because flue gases are often emitted at high temperatures. Therefore, thermal stability of the membrane material decides the membrane performance and the economy of the operation under high temperatures. For such applications, fluorinated polymers are good candidates due to their high hydrophobicity and chemical stability [61].

#### 4. Membrane-absorbent combination

Using gas-liquid membrane contactors for selective separation of gaseous components is an emerging technology. However, when the membrane pores are filled with the liquid (wetted), the mass transfer resistance of the membrane becomes significant [62], resulting into economically unviable operation. Thus long-term stable operation of the membrane contactor requires that the pores of membrane remain completely gas-filled over the prolonged periods of operational time. The wetting tendency of a membrane-absorbent combination is mainly determined by properties of the membrane, the liquid absorbent and their mutual interactions. In general, liquids with low surface tensions tend to wet the surface more as compared to liquids having higher surface tensions. Most of the absorbents used in the acid gases removal are organic in nature and have low surface tension. On the other hand, water with significant surface tension has a relatively low solubility. Hence, there is need for reliable guidelines to select the suitable membrane-absorbent combination for removal of acid gases.

##### 4.1. Wetting characteristics of membrane-absorbent combination

Based on the membrane material and properties, the membrane pores can be theoretically filled with either gas or liquid for the hydrophobic and hydrophilic materials which result in non-wetting mode and overall-wetting mode operation respectively. As it can be seen in Fig. 1a, the membrane pores are completely gas-filled. It is non-wetting mode that happens for hydrophobic membranes. Operation mode for hydrophilic membrane is overall-



**Fig. 1.** Operation modes in a hydrophobic microporous hollow fiber membrane and pore wetting patterns: (a) non-wetting patterns, (b) overall wetting mode and (c) partial-wetting mode [64].

**Table 4**

Surface tension and breakthrough pressure of loaded and unloaded alkanolamine solutions at 295 K [18].

Alkanolamine	CO <sub>2</sub> loading (mol CO <sub>2</sub> /mol amine)	$\gamma_L$ (mN m <sup>-1</sup> )	Breakthrough pressure (kPa)
Water	Unloaded	72.3	25.4
Monoethanolamine(MEA)	Unloaded	68.2	18.2
Diethanolamine(DEA)	Unloaded	64.8	14.4
Methyldiethanolamine(MDEA)	Unloaded	57.2	13.1
Dimethylethanolamine(DMEA)	Unloaded	49.3	12.4
MEA	0.05	69.1	23.0
MEA	0.12	70.2	–
MEA	0.28	72.6	25.5

wetting that the membrane pores remain completely liquid-filled over prolonged periods of operational time (see Fig. 1b). In comparison, the non-wetting mode can obtain the minimal diffusion resistance in the membrane pores [44]. However, even though the membrane used in gas absorption is intensively hydrophobic and able to resist the wetting of absorbents, as it can be seen in Fig. 1c, aqueous absorbent solutions of organic compounds especially alkanolamines can penetrate into partial pores of the hydrophobic membrane and cause partial-wetting [29,31]. The membrane pores will be gradually wetted over prolonged periods of operational time. The partial-wetting mode will make the membrane mass transfer resistance increase rapidly and significantly affect the stability of long-term operation [19,26]. Malek et al. [63] observed the effects of membrane wetting pressures on the overall mass transfer. They assumed that partial-wetting of the membrane can cause a change in the overall mass transfer coefficient in the running of membrane gas absorption. Lu et al. [64] presented a wetting mechanism for the system of hydrophobic hollow fiber membrane-alkanolamine absorbents for CO<sub>2</sub> capture. A mathematical model was developed by correlating the resistance-in-series equation, the Laplace equation and the pore size distribution function of membrane based on the wetting mechanism.

For a given hydrophobic membrane material and structure, the degree of partial-wetting of membrane pores mainly depends on the surface tension and contact angle between the absorbents and the membrane surface besides operating conditions [43]. The minimum pressure (breakthrough pressure) which is applied on the liquid phase to enter the membrane pore can be estimated by the Laplace–Young equation [65,66]:

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

where  $\gamma$  is the surface tension of the liquid,  $\theta$  the contact angle between the fluid phase and the membrane and  $r_{p,\max}$  the maximum membrane pore radius.

In fact, wetting of hydrophobic membrane pores is very complicated due to considerable factors. For example, non-uniform pore sizes can cause different breakthrough pressure in an identical module. In this case, the pores with big sizes are easy to be wetted at a given operation pressure. In addition, in the counter-current operation of the gas and liquid phases in a hollow fiber module, pressure drop over the fiber length can result in the membrane pores wetting of the initial section in the liquid inlet (higher breakthrough pressure) [21]. Moreover, the nature of liquid such as ionic species, complexes, microorganisms or impurities, can change the wetting characteristics of the membrane-liquid system [67].

For a given membrane material and liquid pressure, surface tension of the liquid or concentrations of the active organic compounds in the liquid should be correctly selected to prevent the wetting problem. However, decreasing the absorbent concentration is not a good way to solve the wetting problem. For a given liquid absorbent, an alternative method for increasing the breakthrough pressure is to change the membrane properties. From the Laplace equation, it can be concluded that the breakthrough pressure can be

increased by using membrane with smaller pore size and increasing cosine of contact angle, which can be achieved by enlarging the polarity difference between the liquid and membrane material. The experimental breakthrough pressure and surface tension for a number of aqueous alkanolamine solutions with a PTFE membrane ( $d_{p,\max} = 3.5 \mu\text{m}$ , Schleicher & Schuell) are reported in Table 4.

It should be noted that the maximum pore diameter of the PTFE flat sheet membrane used ( $d_{p,\max} = 3.5 \mu\text{m}$ ) was more than an order of magnitude higher than the pore diameter of the microporous membranes used in the gas absorption experiments (typically 0.1–1  $\mu\text{m}$ ). Therefore, low breakthrough pressure can be attributed to the big pore size of the PTFE membrane although it possesses a hydrophobic structure with good contact angle (generally more than 100°). For polypropylene flat sheet membranes with a pore diameter of 0.2  $\mu\text{m}$ , the breakthrough pressure for the liquids of high surface tension such as water and aqueous salt solutions are larger than the mechanical burst pressure of the membrane [18].

Therefore, in order to prevent wetting in the gas–liquid membrane contactors, it is advisable to operate at a pressure lower than the breakthrough pressure. Some criteria to avoid the wetting problems are suggested by Li and Chen [44].

#### 4.2. Screening of membrane-absorbent combination

Considering the wetting phenomenon, the selection of a membrane-absorbent combination is a critical step in developing gas absorption in the membrane contactors. A key parameter in the screening of potential absorbent solution is the solubility of acid gases. Apart from the solubility, the absorbent should be non-toxic, thermally stable, easily regenerable and commercially available at low cost and should have a low vapor pressure to minimize the losses. The absorbent also should have a low viscosity to avoid high pressure drop over the fiber length. A high viscous solution also reduces the mass transfer rates results in increasing the membrane area requirement. This effect becomes especially noticeable at low temperatures. The most important requirements of absorbent in membrane gas absorption applications are that the long-term use of absorbent should not damage the membrane either physically or chemically and that the membrane-absorbent combination should have sufficiently high critical entry pressure to avoid wetting.

The initial screening of the membrane materials is based on the hydrophobicity of the membrane. Membranes having a high hydrophobicity and low surface energies such as PTFE, polypropylene, PVDF, polysulfone and polyethersulfone usually are selected for gas absorption applications. In order to investigate the compatibility of membranes and absorbents some researches have been conducted [47,53,68]. Dindore et al. [22] selected some membranes and kept them in contact with the different physical absorbents over a period of time. Then the membranes were carefully investigated for the immediate spreading of an absorbent and/or for the damage caused by an absorbent to a membrane. Table 5 shows their results for the compatibility of the absorbents with the membranes in terms of immediate spreading of the absorbent and/or the surface damage of a membrane. As indicated in Table 5 only PTFE

**Table 5**  
Membrane-absorbent compatibility [22].

Solvent	PTFE	PP	PVDF	PES	PS
Water	Yes	Yes	Yes	Yes	Yes
Propylene carbonate	Yes	Yes	No	No	No
Selexol	Yes	No	No	No	No
N-methyl pyrrolidone	No	No	No	No	No
Dimethyl formamide	No	No	No	No	No
Tributyl phosphate	No	No	No	No	No
Glycerol triacetate	Yes	No	No	No	No
n-formyl morpholine	Yes	Yes	No	No	No

and polypropylene membranes were found to be compatible with some of the selected organic absorbents. The rest of the membranes showed incompatibility with the selected absorbents in terms of morphological damage, swelling, shrinkages, color change or dissolution. Therefore, it was decided to use PTFE and polypropylene membranes for further experimental work.

## 5. Hollow fiber membrane modules

In the gas–liquid membrane contactor operations, the membrane performance may be limited less by the membrane resistance than by the resistance of the fluids adjacent to it. This means that successful membrane process design must consider not only membrane chemistry and structure, but also flow configuration and module geometry. As a device that achieves mass transfer in gas–liquid or liquid–liquid system, hollow fiber membrane module has been extensively used in such separation processes as gas absorption/stripping, extraction, membrane distillation, etc. Typically, hollow fiber membrane module is a bundle of porous hollow fibers packed in parallel alignment into a shell, similar in configuration to a shell and tube heat exchanger. In this structure, the fibers are packed randomly on the shell leads to non-uniform fiber distribution. So there may exist severe fluid channeling and bypassing on the shell side of the module result in deterioration of the mass transfer process. In addition, a severe limitation to fluid flow due to small fiber internal diameter can also limit mass transfer at the lumen side. The underperformance of hollow fiber membrane module causes much limitation to its application in industry. Therefore, improving its mass transfer has become an important subject to researchers. By far, many works focusing on this improvement can be found in literatures [14,69,70], with the important given to features such as the regularity of fibers, packing density and the relative flow directions such as parallel, i.e., co-currently and counter currently, and cross-flows of the two phases.

### 5.1. Longitudinal flow module

In these modules, the gas and liquid phases flow in parallel to each other on the opposite side of the fibers. The flows can be co-current or counter-current. Most of the researches on the membrane gas absorption in laboratory scale have conducted on this kind of membrane module [15–31]. Yang and Cussler [71] discussed the construction of the parallel and cross-flow modules. They reported the results of experiments made with these modules, and described the mechanism responsible for controlling the mass transfer in the various cases. Finally, they discussed the correlations that can be inferred from their experiments, and compare these with correlations previously reported for analogous heat and mass transfer problems. Their discussion provides a basis for designing hollow fiber membrane modules for contacting both gases and liquids in other situations.



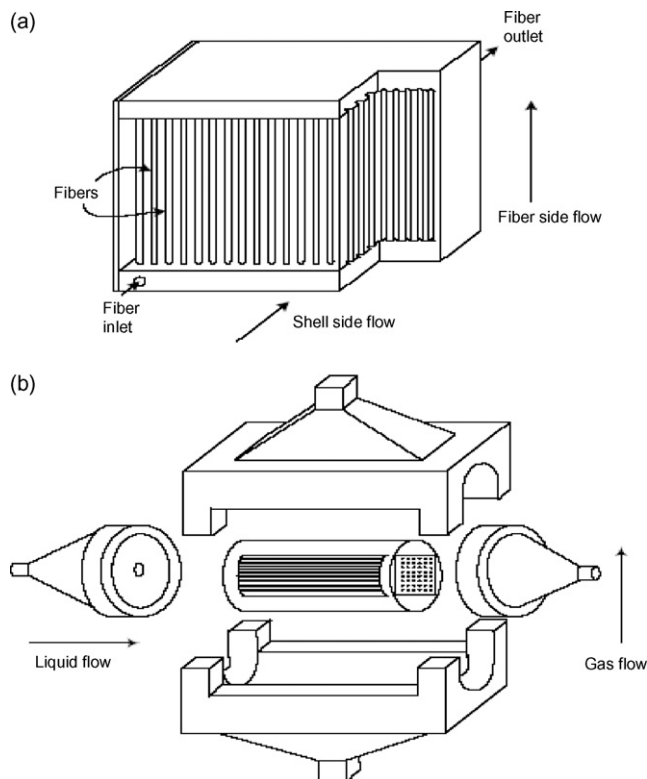
**Fig. 2.** A parallel-flow hollow fiber gas–liquid membrane contactor.

A schematic diagram of this type of module is given in Fig. 2. The simplicity in manufacturing, well known fluid dynamics in shell and tube side and easiness of mass transfer estimation are the advantages of this module, even though its disadvantages is mainly seen in its moderate efficiency in mass transfer compared with the cross-flow module.

### 5.2. Cross-flow module

In general, cross-flow operation of hollow fiber membrane contactors is preferred as it offers several advantages such as higher mass transfer coefficients, minimized shell side channeling and lower shell side pressure drop as compared to the parallel flow contactors. Physical gas absorption in a rectangular cross-flow hollow fiber gas–liquid membrane contactor has been discussed in detail by Dindore and Versteeg [69]. They carried out experiments to study the effect of various parameters such as gas and liquid flow rates, solute concentration in the feed stream on the performance of the rectangular cross-flow gas–liquid membrane contactors. Wickramasinghe et al. [72] also evaluated the performance of different parallel and cross-flow gas–liquid membrane contactors based on the equal flow per membrane area and equal flow per module volume and found that in both cases cross-flow membrane modules were more effective as compared to parallel flow modules.

Fig. 3(a and b) shows two types of cross-flow module. Module (a) was provided by TNO-MEP and module (b) was constructed by Dindore and Versteeg [69].



**Fig. 3.** (a, b) Cross-flow membrane contactor modules [69].

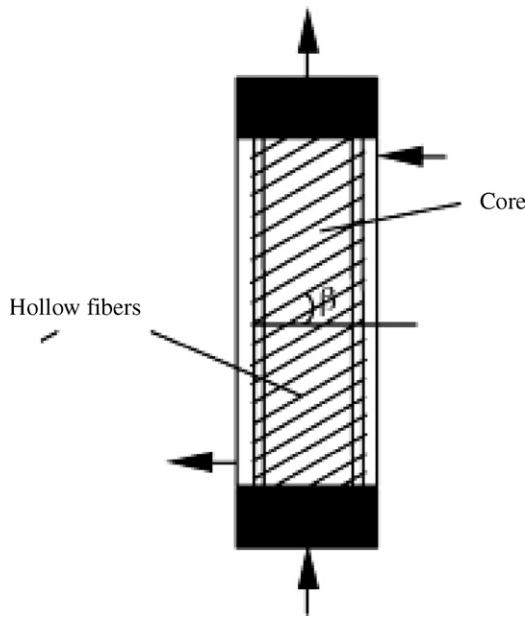


Fig. 4. Schematic representation of coiled module [70].

### 5.3. Coiled module

Recently, more attention is paid to the coiled modules for the ultrafiltration and nanofiltration membrane applications [73–75]. In this module curved channels are used to create secondary flow (Dean Vortices) in fluid, so that the involved flow and transfer process are intensified. One important advantage of coiled module over other techniques is its capability of simultaneous improvement on mass transfer in both lumen and shell side. Liu et al. [70] prepared coiled hollow fiber membrane modules and examined their mass transfer performances for stripping dissolved oxygen from water. It was found that, compared with the conventional straight module, the mass transfer in both tube and shell side of the coiled hollow fiber module could be remarkably enhanced. The improvements in mass transfer can be attributed to the created secondary flows (known as Dean Vortices) inside coiled fiber and the promoted turbulence on the shell. Moulin et al. [76] studied a helically wound hollow fiber (or tubular) membrane module in an oxygenation operation with water flowing in the laminar regime inside the tube. The data was compared with a conventional module where straight hollow fiber membranes were in parallel alignment. It was shown that the presence of vortices gives better performance in terms of oxygen transfer. Improvement factors were in the range of 2–4. Therefore, this kind of module can be considered as an alternative to improve the mass transfer in hollow fiber gas–liquid membrane contactors. However, the number of researches on this area is rare. Fig. 4 presents schematic of the coiled module.

## 6. Mass transfer in membrane contactors

Membrane gas absorption is based on a gas–liquid contact across a hydrophobic porous membrane which permits mass transfer between the two phases without dispersing one phase into the other. Generally, the gas fills the hydrophobic membrane pores and meets the liquid at the opposite side of the membrane. The liquid phase pressure should be slightly higher than that of the gas phase to prevent dispersion of gas bubbles into the liquid. As long as the excess absorbent solution pressure is less than the breakthrough pressure of the membrane the solution does not penetrate into the

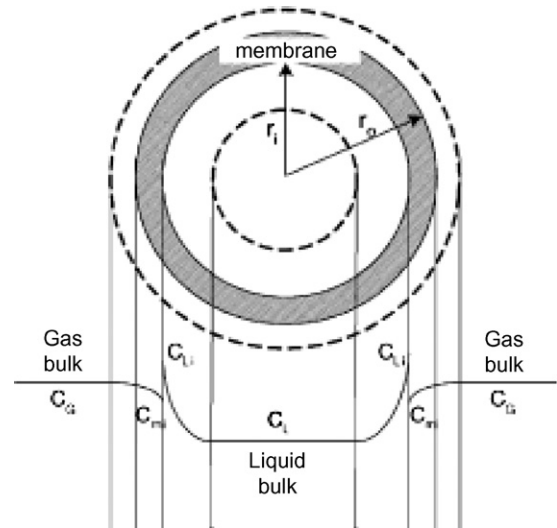


Fig. 5. Mass transfer process in a hollow fiber membrane gas/liquid contactor [21].

pores and the gas–liquid interface is immobilized at the pore mouth of the membrane on the liquid side.

Operation of gas–liquid membrane contactors differs from that of other membrane processes such as filtration, since there is no convective flow through the pores and only diffusive transport of certain components happen. This is the main reason that membrane contactors are less sensitive to fouling than conventional membranes. As the membrane is non-selective, the chemistry of the separation is the same as that for conventional equipment. The choice of a suitable combination of absorption liquid, membrane characteristics and operation mode determines the selectivity of the process.

In order to describe a gas absorption into a liquid flowing through a hollow fiber membrane the resistance in series model can be used. Fig. 5 shows the mass transfer process in a hollow fiber gas–liquid membrane contactor.

The overall process consists of three steps. First, the transfer of the solute gas from the bulk gas phase to the membrane surface. Second, transfer through the membrane pores and last, the transfer from the membrane–liquid interface into the bulk of the liquid. Therefore, for a hydrophobic hollow fiber membrane with gas-filled pores and liquid absorbent in the lumen side, the overall liquid phase mass transfer coefficient ( $K_o$ ) can then be expressed by a resistance in series model [19,43,51]:

$$\frac{1}{K_o} = \frac{m}{k_g d_o / d_i} + \frac{m}{k_m d_{lm} / d_i} + \frac{1}{E k_l} \quad (2)$$

where  $k_g$ ,  $k_m$  and  $k_l$  are the individual mass transfer coefficients (m/s) of gas phase, membrane and liquid phase, respectively;  $d_o$ ,  $d_i$  and  $d_{lm}$  are the outer, inner and log mean diameters of hollow fiber membrane (m);  $m$  is the distribution coefficient between gas and liquid phase (–); and  $E$  is the enhancement factor due to chemical reaction (–).

For gas absorption, the resistance to gas diffusion from the bulk gas to the membrane external surface can be ignored compared to other resistances [3,9,21]. In the case of physical absorption such as carbon dioxide in water the resistance connected with the liquid phase should depend on experimental hydrodynamics and it needs to remain unchanged for a constant liquid flow rate.

The membrane resistance depends on membrane mode of operation, i.e. non-wetted, wetted or partially wetted mode. For totally gas-filled pores or totally liquid-filled pores, the membrane resistance depends on the diffusivity of the absorbing gas in the gas phase,  $D_{g,eff}$ , or in the liquid phase,  $D_l$ , respectively, and on the



geometrical characteristics of the membrane, i.e. its thickness,  $l_m$ , porosity,  $\varepsilon_m$  and tortuosity,  $\tau_m$  [33,62]. Non-wetted mode is the superior mode of operation for gas absorption in the membrane contactor that can minimize the membrane resistance. In order to prevent wetting, some criteria such as balanced gas–liquid operating pressure, using highly hydrophobic membrane materials, high surface tension liquid absorbent and optimized membrane structure with small pore size can be taken into consideration.

Generally, longitudinal membrane contactor modules are used for gas absorption where the liquid flows through the lumens of the fibers and the gas flows in shell side of the module. Therefore, our next focus will be on the membrane, shell side and tube side mass transfer.

### 6.1. Membrane mass transfer

In some gas absorption cases, the absorption rate is mainly controlled by diffusion across the membrane. Qi and Cussler [33] studied  $\text{NH}_3$  absorption in water,  $\text{H}_2\text{S}$  and  $\text{SO}_2$  separately into aqueous NaOH and found that the membrane resistance to mass transfer in the case of air– $\text{NH}_3$ –water system is about 85% of total resistance. However, their data on  $\text{CO}_2$  absorption in aqueous NaOH or aqueous amine solutions show that the main resistance to mass transfer lies in the liquid phase, with membrane resistance being very small. They also stated that, for cases where membrane resistance is relatively small, hollow fiber membrane module has a distinct advantage over the conventional packed column.

The membrane resistance depends on membrane mode of operation (non-wetted, wetted or partially wetted). In the non-wetted (gas-filled pores) and wetted (liquid filled pores) cases, the membrane mass transfer coefficients ( $k_{mg}$  and  $k_{ml}$ ) are given by the following equations respectively.

$$k_{mg} = \frac{D_{g,\text{eff}}\varepsilon_m}{\tau_m l_m} \quad (3)$$

$$k_{ml} = \frac{D_l \varepsilon_m}{\tau_m l_m} \quad (4)$$

The effective diffusion coefficient of gas in the non-wetted pores,  $D_{g,\text{eff}}$ , is determined by the interactions between the molecules (molecular diffusion) as well as the interactions of the molecules with the walls of the pore (Knudsen diffusion).

The molecular self-diffusion coefficient of the gas,  $D_{g,m}$  ( $\text{m}^2/\text{s}$ ), is calculated from the kinetic gas theory [77,78]:

$$D_{g,m} = 1200 \left( \frac{RT}{MP} \right) \left( \frac{\Omega_\mu}{\Omega_D} \right) \mu \quad (5)$$

Where  $M$  is the gas molecular weight and  $\mu$  is the gas dynamic viscosity in (Pa s). The collision integrals  $\Omega_\mu$  and  $\Omega_D$  are dimensionless functions of temperature and they are calculated from the Neufeld et al. empirical equations [78]. The Knudsen diffusion coefficient of the gas,  $D_{g,\text{Kn}}$  ( $\text{m}^2/\text{s}$ ), is obtained from Ref. [79]:

$$D_{g,\text{Kn}} = 0.97 r_p \left( \frac{T}{M} \right)^{0.5} \quad (6)$$

Where  $r_p$  is the pore radius in cm. The effective diffusion coefficient of the gas in the gas-filled membrane pores,  $D_{g,\text{eff}}$  ( $\text{m}^2/\text{s}$ ), is estimated using the following equation [60]:

$$D_{g,\text{eff}} = \left( \frac{1}{D_{g,m}} + \frac{1}{D_{g,\text{Kn}}} \right)^{-1} \quad (7)$$

The diffusion coefficient of the gas in the pores filled with the liquid absorbent,  $D_l$ , is determined by the interactions between the molecules.  $D_l$  ( $\text{m}^2/\text{s}$ ), can be estimated using Versteeg and Van

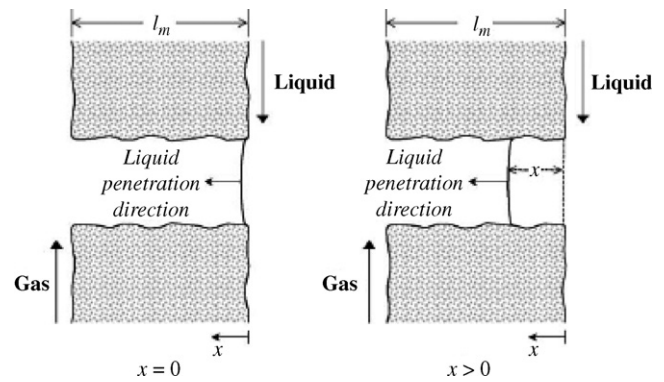


Fig. 6. Membrane pore partial-wetting by liquid [80].

Swaaij equation [79]:

$$D_1 = 2.35 \times 10^{-6} \exp \left( -\frac{2119}{T} \right) \quad (8)$$

For partially wetted pores, the membrane resistance is a function of the resistance of pores filled with gas, the resistance of pores filled with liquid and the wetting ratio,  $x^*$ , i.e. the pore length wetted by liquid,  $x$ , to the overall pore length,  $l_m$ , shown schematically in Fig. 6. When the liquid intrusion into the membrane pore increases with time, the ratio  $x^*$  also changes, and consequently, the membrane mass transfer coefficient,  $k_m(t)$ , will change according to [80]:

$$k_m(t) = \frac{1}{\left( \frac{1-x^*(t)}{k_{mg}} + \frac{x^*(t)}{k_{ml}} \right)} \quad (9)$$

$k_{mg}$  and  $k_{ml}$  are the mass transfer coefficient values of the totally gas-filled and the totally liquid-filled membrane pores, defined by Eqs. (3) and (4), respectively.

It is to be noted that these equations are based on the assumption that the membrane characteristics are constant. However, using the above equations to predict the membrane coefficient may lead to large errors for membranes with a large pore distribution. Studies showed that for a membrane with a smaller average pore size and a higher standard deviation in pore-size distribution, significant error in membrane's coefficient can be caused by the pore-size distribution [82]. This is because, as the average pore size decreases, the membrane's coefficient is progressively dominated by the Knudsen diffusion coefficient. Under this regime, the pore-size distribution has a great effect on the membrane's coefficient. It is also worth mentioning that the effect of membrane porosity on the separation process seems to be insignificant [63].

It was observed that although the gas was only in contact with the liquid at the pore entrances, the total membrane area had to be used for the determination of mass transfer coefficient. This is because the distance between the pores is extremely small compared to the fiber diameter. In fact, in previous studies, the total membrane area is generally assumed as the overall gas–liquid interfacial area.

### 6.2. Shell side mass transfer

One of the most commonly used hollow fiber geometries is the shell and tube configuration with a bundle of hundreds of porous fibers, aligned axially in the cross-section. However, the performances of these modules vary significantly. This can be caused by a number of factors. Some of the possible causes include the irregularity of fiber spacing within the module, polydispersity of fiber diameters, fiber movement during operation, influence of the wall of the module and inlet and outlet effects. The fibers can be packed in the shell side uniformly or randomly. A number of studies have

**Table 6**  
Shell side mass transfer correlations for hollow fiber membrane modules.

Flow	Correlation	Condition	Reference
Parallel	$Sh = 1.25(Re d_h/L)^{0.93} Sc^{0.33}$	$0.5 < Re < 500; \varphi = 0.03$	[71]
	$Sh = 5.85(1 - \varphi)(d_h/L) Re^{0.6} Sc^{0.33}$	$0 < Re < 500; 0.04 < \varphi < 0.4$	[87]
	$Sh = (0.53 - 0.58\varphi) Re^{0.53} Sc^{0.33}$	$21 < Re < 324; 0.32 < \varphi < 0.76$	[85]
	$Sh = (0.3045\varphi^2 - 0.3421\varphi + 0.0015) Re^{0.9} Sc^{0.33}$	$32 < Re < 1287; 0.1 < \varphi < 0.7$	[88]
Cross	$Sh = 1.38Re^{0.34} Sc^{0.33}$	$1 < Re < 25; \varphi = 0.7$	[71]
	$Sh = 0.90Re^{0.40} Sc^{0.33}$	$1 < Re < 25; \varphi = 0.07$	[71]
	$Sh = 0.61Re^{0.363} Sc^{0.333}$	$0.6 < Re < 49; \varphi = 0.003$	[89]

<sup>a</sup>  $d_h$  is hydraulic diameter (m) and  $L$  is module length (m).

been carried out on the theoretical background of mass transfer, heat transfer and fluid dynamics in the case of uniform distribution of solid rod and hollow fiber arrays [80,81]. However, it has been long recognized that uniform fiber distribution is an unrealistic assumption for most hollow fiber modules, and that channeling of the fluid through the maldistributed hollow fibers is often experienced in shell-side flow [83–87].

Shell side mass transfer performances of various contactor configurations have been calculated for parallel and transverse flow across the fibers to compare the efficiency of the modules. Physical mass transfer has been accounted by the form of  $Sh = f(\varphi, Re^a, Sc^b)$ . Where  $\varphi$  is packing density and  $Re$ ,  $Sc$  are Reynolds and Schmidt number, respectively. Shell side mass transfer correlations for hollow fiber modules have been determined in a number of studies. Table 6 presents some mass transfer correlations for shell side flow parallel and across the fibers.

### 6.3. Tube side mass transfer

In the case of a liquid flowing through lumen of the hollow fiber, mass transfer can be estimated accurately if the exact hydrodynamics near the interface is known. Due to the very small diameter of fibers, the liquid flow is in the laminar region ( $Re < 2100$ ) therefore the hydrodynamic conditions near the interface are well known. A set of differential equations and boundary conditions can be obtained from the mass balance inside the fibers when the external mass transfer resistance is very small and can be negligible and if equilibrium exists at the gas–liquid interface. The solution can be derived using the method suggested by Leveque and Graetz [90,91]. The local value of Sherwood number in terms of Graetz solution and average Sherwood number were obtained as series equations. The series in the equation for local Sherwood number converges rapidly for small values of Graetz number,  $Gz = (u_i d_i^2 / D_1 L)$  so that only first term in the series is significant. Under these asymptotic conditions the average Sherwood number is given by:

$$Sh = \frac{k_1 d_i}{D_1} = 3.67 \quad Gz < 10 \quad (10)$$

Another asymptotic solution is given by the Leveque equation by assuming that the concentration boundary layer is restricted to a thin zone near the wall of the fiber. This approximation is valid in cases of high mass velocities through relatively short fibers in laminar flow. One important consequence of this assumption is that the Leveque solution is only applicable for  $Gz$  numbers exceeding 20. The Leveque solution is given by:

$$Sh = 1.62(Gz)^{1/3} \quad Gz > 20 \quad (11)$$

It has been shown by many researchers that for systems using aqueous solutions at atmospheric pressure; Graetz–Leveque solution can be used to predict the fiber side mass transfer coefficient. Kreulen et al. [6] gave the generalized solution of Graetz–Leveque equation by curve fitting of Eqs. (10) and (11), which is also valid

for the transition region not covered by Eqs. (10) and (11):

$$Sh = (3.67^3 + 1.62^3 Gz)^{1/3} \quad 10 < Gz < 20 \quad (12)$$

Graetz–Leveque equations overestimate experimentally determined mass transfer coefficients at low flows; this can be attributed to non-uniform flow caused by polydispersity in hollow fiber diameter [73]. Park and Chang [92] showed that tube side flow distribution is often not uniform. Using high-speed photography and dye tracer studies, these researchers determined that the distribution depends on the inlet manifold type (cylindrical or conical), manifold height, tube length, fiber inner diameter, shell diameter, fiber packing density and Reynolds number. Wickramasinghe et al. [72] assumed a Gaussian distribution of fiber radii, then integrated the basic equation for the mass transfer coefficient over all radii and obtained the following power series solution for the average tube side coefficient:

$$\bar{Sh} = Sh[1 - (18Sh/Gz + 7)e_0^2 + \dots] \quad (13)$$

Here  $\bar{Sh}$  is the average Sherwood number,  $Sh$  is the Sherwood number expected for a uniform distribution of fiber radii,  $Gz$  is the Graetz number and  $e_0^2$  is the standard deviation of fiber radii divided by the mean. Eq. (13) was developed for low flow conditions, i.e., the Graetz number less than four; at these low flows, the quantity in brackets is less than one. Since the distribution of fiber diameters leads to low flows in some fibers, as a result, polydispersity can lead to a reduction in the mass transfer coefficient.

### 6.4. Mass transfer with chemical reaction

As in any mass transfer device, chemical reaction can have a major effect on the rate of mass transfer in membrane contactors. Considering gas–liquid mass transfer, in the absence of chemical reaction, the gas phase resistances are usually negligible and the liquid boundary layer resistance controls mass transfer. However, if a chemical reaction occurs between the absorbed gas species and the solvent, the liquid side resistance is reduced and the gas phase resistance may actually control mass transfer [7,15]. So, the mass transfer can be enhanced when chemical reactions are present. The enhancement factor ( $E$ ) describes the effect of chemical reaction on the mass transfer rate. Generally, the enhancement factor is defined as the ratio of absorption flux in presence of chemical reaction (chemical absorption) to the absorption flux in absence of chemical reaction (physical absorption) for identical mass transfer force:

$$E = \frac{J_{chem}}{J_{phy}} \quad (14)$$

The enhancement factor affects the mass transfer rate significantly and thus the design of membrane gas–liquid contactors will be the subject of further discussion.

Several approximate solutions to predict the enhancement factor based on different mass transfer models (film, penetration and surface renewal) are available in the literature and are applicable

over a wide range of process conditions with different reactions and chemical solute loading. Kumar et al. [93] measured the absorption flux and enhancement factor in the single fiber membrane contactor, as it is described in their work, these features are very well predicted by the numerical model as well as the adapted DeCoursey's approximate solution [94,95]. Since the hydrodynamics of the liquid flowing inside the hollow fiber of a single fiber membrane contactor is well defined (like in a laminar jet or wetted wall column), they supposed it can also be used as a model gas–liquid contactor.

The Graetz number is the ratio of the penetration time of the solute gas to reach the axis of the hollow fiber (from the gas–liquid interface) to the average residence time of the liquid in the fiber. Depending upon the Graetz number, the mass transfer zone in the liquid phase of the hollow fiber may actually extend up to the axis of the fiber and the centerline concentration may be disturbed. Under the limiting condition of short gas–liquid contact time (high Graetz number), the penetration depth of the gas phase species diffusing from the gas–liquid interface is small in comparison to the fiber radius. Consequently, the liquid far from the interface is essentially undisturbed (analogous to the liquid bulk that is assumed to be present at infinite distance from the gas–liquid interface in traditional mass transfer models) and the concentration of the liquid phase reactant 'B' at the centerline (axis) is the same as the concentration of 'B' in the liquid entering the fiber. Hence at higher Graetz numbers  $\psi$  ( $Gz > 1000$ ), the enhancement factor in the case of gas absorption in a liquid flowing through a hollow fiber can be given by the traditional mass transfer theories. At this case, the dimensionless Hatta number and asymptotic enhancement factor, adopted for a hollow fiber can be described based on surface renewal theory and the conditions at the liquid inlet ( $z = 0$ ):

$$E = Ha^* = \frac{\sqrt{k_{m,n} D_A C_{A,i}^{m-1} C_{B,0}^n}}{k_L} \quad (15)$$

where  $m$  and  $n$  are the partial reaction order with respect to 'A' and 'B' respectively and  $k_{m,n}$  is the reaction rate constant.  $D_A$  and  $C_{A,i}$  are the diffusion coefficient and concentration of specie 'A' to the liquid and  $C_{B,0}$  is the concentration of specie B in the inlet of fiber. The mass transfer coefficient for the laminar flow conditions ( $k_L$ ) was estimated using the Leveque's solution (Eqs. (10–12)). For example, for mass transfer followed by a first-order irreversible chemical reaction, the local reaction rate is proportional to the concentration of the dissolved gas 'A' as  $R_A = -k_1 C_A$ , the asymptotic approximate solution for the enhancement factor in fast reaction regime ( $Ha > 2$ ) is given by:

$$E = Ha^* = \frac{(k_1 D_A)^{1/2}}{k_L} \quad (16)$$

where  $k_1$  is the first-order reaction rate constant,  $k_L$  and  $D_A$  are mass transfer coefficient and diffusion coefficient in the liquid, respectively.

At low Graetz numbers the penetration depth and consequently the reaction zone may extend up to the axis of the fiber. Therefore, the absorption regime can continuously change from the liquid entrance to the liquid exit, in which, the absorption regime over the entire fiber can be assumed as instantaneous reaction regime. In this case, the enhancement factor is given by modified asymptotic infinite enhancement factor:

$$E_\infty^* = \left(1 + \frac{C_{B,0} D_B}{\nu_B C_{A,i} D_A}\right) \left(\frac{D_A}{D_B}\right)^n \quad (17)$$

where  $\nu_B$  is the stoichiometric coefficient of component 'B' in the reaction and  $D_B$  is the diffusion coefficient of species 'B' in the liquid. The above definition neglects the drift convective flow caused by the diffusion of solute gas 'A'. This is in line with the assumptions

associated with the Fick's law, which is the basis for the definition. The value of  $n$  varies depending upon the type of mass transfer model chosen and is given as below:

Film model:  $n = 0$ ; Penetration model:  $n = 1/2$ ; Leveque model (presence of a velocity gradient in the mass transfer zone):  $n = 1/3$ .

For the general case the approximate enhancement factor, based on DeCoursey's solution [93,94] (using the definition of modified Hatta number and modified infinite enhancement factor), is given by:

$$E_{app} = \frac{-(Ha^*)^2}{2(E_\infty^* - 1)} + \sqrt{\left[\frac{(Ha^*)^2}{4(E_\infty^* - 1)^2} + \frac{E_\infty^* (Ha^*)^2}{(E_\infty^* - 1)} + 1\right]} \quad (18)$$

In the case of very low Graetz number, the species 'B' is completely consumed by the reaction over a certain portion of the fiber and then species 'A' starts physically absorbing into the liquid phase containing the reaction product till it is saturated with the species 'A'. In such cases, the enhancement due to the chemical reaction is entirely determined by the stoichiometric coefficients and the concentrations of species 'A' and 'B'.

### 6.5. Experimental mass transfer coefficient

A general schematic diagram of experimental set up is shown in the Fig. 7 in which by running the experimental system the required parameters will be obtained to calculate overall and individual mass transfer coefficients according to the resistance-in-series model. The overall mass transfer coefficient,  $K_{overall}$ , based on liquid phase is calculated by Eq. (19):

$$K_{overall} = \frac{Q_L (C_{L,out} - C_{L,in})}{A (\Delta C)_{Lm}} \quad (19)$$

where  $Q_L$  is the liquid flow rate,  $C_{L,out}$  and  $C_{L,in}$  are the liquid phase outlet and inlet concentration of the acid gas respectively,  $A$  is the gas–liquid contact area and  $(\Delta C)_{Lm}$  is the logarithmic mean driving force based on liquid phase concentration:

$$(\Delta C)_{Lm} = \frac{(C_{L,in}^* - C_{L,out}) - (C_{L,out}^* - C_{L,in})}{\ln[C_{L,in}^* - C_{L,out} / C_{L,out}^* - C_{L,in}]} \quad (20)$$

The  $C_{L,in}^*$  and  $C_{L,out}^*$  hypothetical liquid phase concentrations in equilibrium with the corresponding gas phase concentration,  $C_g$ , expressed by Henry's law as:

$$C_L^* = H_i C_g \quad (21)$$

where  $H_i$ , the Henry's law constant, can be obtained from the literature or determined experimentally. Typically, the feed concentration and the interfacial area are known, so that measurement of the flow rate and outlet concentrations allows the mass transfer coefficient to be calculated.

As an alternative to Eq. (3), the Wilson plot method can be used to determine the membrane resistance, and also to identify the effect of fluid velocities on individual mass transfer coefficients. By assuming that the individual coefficients for the gas and liquid boundary layers are proportional to  $\mu_1^\alpha$  where  $\alpha$  is an empirical constant, the Wilson plot is drawn by  $1/K_{overall}$  versus  $1/\mu_1^\alpha$  based on Eqs. (2) and (11). The value of  $\alpha$  is chosen for achieving the best straight line. In the gas–liquid membrane contacting process, if the resistance in the gas phase is much smaller than the overall resistance (low solubility of gas component, using pure gas and/or a high gas flow rate) the gas phase resistance in Eq. (2) becomes negligible. Thus, the interception of the Wilson plot represents the value of membrane mass transfer resistance. Atchariyawut et al. [51] showed the Wilson plot for the four types of PVDF membranes (Fig. 8). They indicated the effect of membrane structure on the performance  $CO_2$  absorption by pure water.

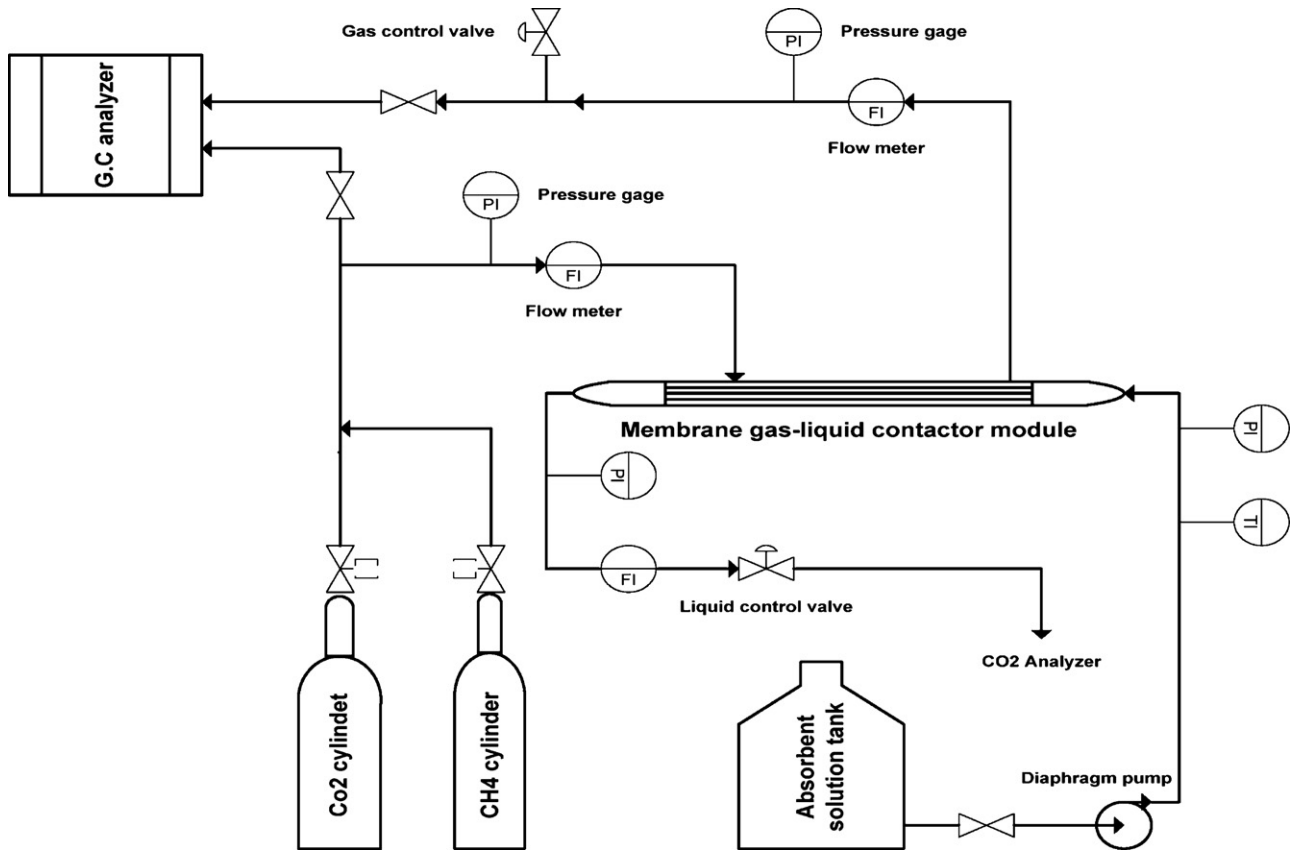


Fig. 7. Schematic diagram of experimental set up.

7. Mathematical model development

The hollow fiber modules used in literature are generally configured in parallel that the gas and liquid flow on the opposite sides of the membrane. The gas phase can flow either outside (shell) or inside (lumen) of the hollow fiber membrane. However, in most of the studies the liquid phase was designed to flow in the lumen. The advantage is that the dimension of the lumen channels can be easily defined and it is easier to get numerical solutions. Several theoretical models have been developed to describe acid gas absorption in membrane contactors that the liquid absorbent has been assumed to flow in the lumen of the membrane while the gas flows in the shell side [23,27,95–97]. Following assumptions have been considered:

(1) A steady state and isothermal condition have been achieved.

- (2) Laminar parabolic velocity profile is used in the lumen of fibers.
- (3) The axial diffusion is negligible.
- (4) Ideal gas behavior is valid for gas phase.
- (5) Henry's law is applicable for interface concentrations.

Subject to these assumptions, main equations for gas absorption in a hollow fiber membrane contactor can be derived.

7.1. Liquid phase equations

Based on the assumptions the conservation equation for the mass transfer in the liquid phase can be derived as:

$$u \frac{\partial C_i}{\partial Z} = D_i \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_i}{\partial r} \right) \right) - R_i \quad 0 < r < r_i \tag{22}$$

Where *i* denotes the components (solute and absorbent). *D*, *C*, *R*, *r* and *Z* denotes the diffusion coefficient, concentration, reaction rate, radial coordinate and axis coordinate, respectively. The quantity *u* is the axial velocity profile. In the hollow fibers, a laminar parabolic velocity profile is:

$$u = 2\bar{u} \left( 1 - \left( \frac{r}{r_i} \right)^2 \right) \tag{23}$$

where  $\bar{u}$  is the average flow velocity, *r* the radial distance, and *r<sub>i</sub>* is the fiber inner radius. The initial and boundary conditions are:

$$Z = 0, \quad C_{A1} = 0, \quad C_B = C_{B0} \tag{24}$$

$$r = 0, \quad \frac{\partial C_{A1}}{\partial r} = 0 \quad \frac{\partial C_B}{\partial r} = 0 \tag{25}$$

$$r = r_i, \quad C_{A1} = HC_{Am,i} \quad \frac{\partial C_B}{\partial r} = 0 \tag{26}$$

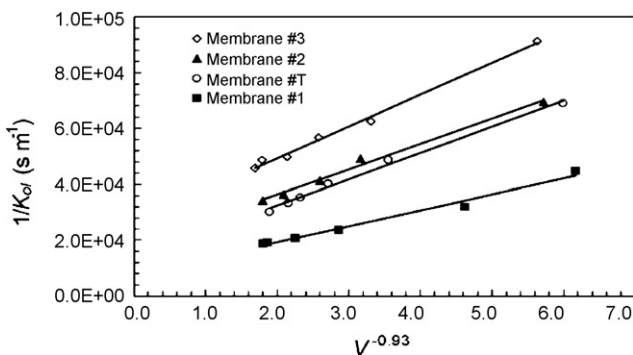


Fig. 8. Wilson plot of four different PVDF membranes (pure CO<sub>2</sub>–pure water system) [51].

where the subscripts 'A' and 'B' denote solute component and absorbent, respectively and symmetry in the radial direction of hollow fibers and non-volatile absorbent assumed. The Henry's law is applied to connect the solute component interfacial concentration in the liquid and membrane phase.

### 7.2. Gas phase equations

The gas flow in the shell side of the membrane contactor can be configured as fluid envelopes around the fiber and there is no interaction between fibers. A similar mass conservation equation can be given as follows:

$$u \frac{\partial C_A}{\partial Z} = D_{A,g} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_A}{\partial r} \right) \right) \quad r_o < r < r_e \quad (27)$$

It is suggested that Happel's free surface model [98] can be used to characterize the out fibers velocity profile. Although the flow in the real hollow fiber modules is not absolutely according with Happel's model, it has been extensively used for the membrane contactor [19,16]. The laminar parabolic velocity profile in the outside fibers is:

$$u = 2\bar{u} \left( 1 - \frac{r_o}{r_e} \right) \times \left( \frac{\left( \frac{r}{r_e} \right)^2 - \frac{r_o}{r_e} + 2 \ln \left( \frac{r_o}{r} \right)}{3 + \left( \frac{r_o}{r_e} \right)^4 - 4 \left( \frac{r_o}{r_e} \right) + 4 \ln \left( \frac{r_o}{r_e} \right)} \right) \quad (28)$$

where  $r_e$  and  $r_o$  are the radius of free surface and fiber outer radius, respectively.  $r_e$  represents a fluid envelope across each fiber which there is no mass or momentum transfer. It can be defined as:

$$r_e = \left( \frac{1}{1 - \phi} \right)^{1/2} r_o \quad (29)$$

In which,  $\phi$  is the shell side packing fraction of module. It can be calculated as follows:

$$\phi = \frac{n r_o^2}{r_s^2} \quad (30)$$

Where  $n$  is the number of fibers and  $r_s$  is the module inner radius.

The boundary condition of Eq. (27) is:

$$r = r_o \quad Z = z \quad C_{Ag} = C_{Am} \quad (31)$$

$$r = r_e, \quad Z = z \quad \frac{\partial C_{Ag}}{\partial r} = 0 \quad (32)$$

### 7.3. Membrane phase equations

Within the membrane phase, the diffusion phenomenon is described as:

$$D_{Am} \left( \frac{\partial^2 C_{Am}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{Am}}{\partial r} \right) = 0 \quad r_i < r < r_o \quad (33)$$

The boundary conditions of Eq. (33) are:

$$r = r_i \quad C_{Al} = HC_{Am} \quad (34)$$

$$r = r_o \quad C_{Am} = C_{Ag} \quad (35)$$

Differential Eq. (33) subject to boundary conditions can be solved and the concentration profile at the membrane is found to be:

$$\frac{C_{Am} - C_{Al}/H}{C_{Ag} - C_{Al}/H} = \frac{\ln(r/r_i)}{\ln(r_o/r_i)} \quad (36)$$

Due to the difficulty in solving the differential of Eqs. (22) and (27) by analytical method for the gas component in the tube and shell sides, numerical methods such as finite difference or finite element have been employed to determine the concentration profiles in the tube and shell sides.

## 8. Advantages of gas–liquid membrane contactors over the other gas separation methods

In a gas–liquid membrane contactor, membrane separation is not only combined with an absorption process but both processes are fully integrated into one piece of equipment. In this way advantages of both processes can be fully achieved. The membrane offers a flexible modular energy efficient device with a high specific surface area. The absorption process can offer a very high selectivity and a high driving force for transport even at very low concentrations [99]. Therefore, hollow fiber gas–liquid membrane contactor is able to remove acid gas from gas streams with extreme variations in gas flow and/or concentrations of the components. This, results in low weight and very compact equipment.

The dense membranes which are usually nonporous have been used for acid gas separation at relatively high pressure. However, commercial utilization of gas separation membranes is still somewhat limited due to low permeability and low separation factors. Furthermore, at low acid gas concentration, driving force for gas separation is reduced and significant amount of the main gas is lost in the permeate side. The problem becomes even more severe when acid gases need to be separated simultaneously. In comparison, gas–liquid membrane contactors possess higher selectivity and removal efficiency even at very low acid gas concentrations without any loss of the main gas.

In gas–liquid membrane contactors, the gas and liquid flow are independent compare to conventional absorber. Therefore, it is easy to achieve a flexible operation without entrainment, flooding or foaming. And also, it gives an optimum load of liquid absorbent. The surface contact per unit volume is very high, known and constant that allowing the performance to be predicted more easily than the conventional absorption system like packed columns, where the surface area per unit volume may be known, but it is often difficult to determine the specific surface area (see Table 1). In addition, scaling-up is more straightforward. The operation usually scales linearly, so that a predictable increase in capacity is achieved simply by adding new membrane modules. Generally, the successful use of the hollow fiber gas–liquid membrane contactor over the conventional absorption processes will depend on the gas–liquid system, the properties of membranes used and the operating conditions [30].

Gas absorption comparisons between packed columns and membrane contactor systems have been reported in the literature by several authors [3,5,9,100]. deMontigny et al. [101] conducted a more accurate performance comparison between these two contacting devices with considering operating conditions, using packed column containing structured packing. Their results showed that changes in the gas flow rate, liquid flow rate, and solution concentration affected gas absorption in the membrane contactors and packed columns in the same manner. Moreover, the membrane contactor produced mass transfer values that were up to four times larger than the values obtained in a packed column containing Sulzer DX structured packing.

Through the use of hollow fiber membranes for acid gas capture, membrane gas absorption process offers several economical advantages over conventional gas absorber column including: low investment costs, low pumping power, expensive civil engineering work is not necessary, etc. Although, so many researches have been conducted on the economic analysis of acid gas capture system using conventional absorber or gas separation membranes [102–104], economic analysis of membrane gas absorption technology is very rare in the literature. Yan et al. [105] compared the CO<sub>2</sub> absorption performance of a membrane gas absorption system and chemical absorption system based on the overall mass transfer coefficient. Their results showed that if the fresh membranes were tested, the membrane contactor has the higher mass transfer val-

ues than that of the randomly packed column. However, when all the membrane pores were completely wetted, the packed column performs better than the membrane contactor. In addition, results of economic analysis indicated that if the real operational time of membrane module is reduced to less than the critical value affected by the membrane price, the CO<sub>2</sub> captured cost of the membrane gas absorption system is inversely higher than that of chemical absorption system. Therefore, considering better results for membrane gas absorption systems compare to conventional absorber may be somewhat arbitrary unless membrane pore-wetting problems.

### 9. Disadvantages of gas–liquid membrane contactor

Although, gas–liquid membrane contactors offer many advantages over conventional gas absorption systems, there is some disadvantages and technical hurdles that more works are required to properly evaluate the technology in acid gas absorption service. The presence of a membrane itself adds another resistance to the mass transfer process which is not encountered in absorption columns. This resistance could negatively affect the overall mass transfer and significantly lower the selectivity. This membrane resistance can be minimized by reducing the membrane thickness or by increasing its surface porosity (gas permeability). Many authors have particularly investigated this point [58,106,107]. In addition, membrane resistance can be more important if the membranes are wetted by the liquid absorbent. Wang et al. [26] investigated influence of membrane wetting on CO<sub>2</sub> capture in hollow fiber membrane contactors and the results showed that the reduction of overall mass transfer coefficient may reach 20% even if the membrane pores were 5% wetted. The membrane wetting by absorbents has become a great concern for the practical application of the technology which results in economically unviable operation.

Generally, in gas–liquid membrane contactors, hollow fiber membranes are packed randomly in parallel alignment into a shell, similar in configuration to a shell and tube heat exchanger. The non-uniform fiber distribution can cause severe fluid channeling and bypassing on the shell side of the module which result in decline of the mass transfer process. Moreover, a severe limitation to fluid flow due to small fiber internal diameter can also limit mass transfer at the lumen side. These underperformances are often attributed to its disadvantages in configuration that cause much limitation to its application in industry. Therefore, successful gas–liquid membrane contactor design must consider not only membrane chemistry and structure, but also flow configuration and module geometry.

In addition to membrane characteristics and module configuration, operating conditions such as pressure and temperature of the liquid absorbent, gas and liquid flow rate and concentration can also affect the membrane gas absorption performance significantly. The liquid side pressure should be kept higher than that of the gas side in order to prevent bubble formation in the liquid side in the hollow fibers which results in loss of gas components and operating stability [37,63]. However, a higher pressure in the liquid side can lead to membrane wetting in long-term operation. Although, an increase in the absorbent liquid temperature can increase the reaction rate in chemical absorption, it may decrease the liquid surface tension considerably that results in easier membrane wetting or can cause change in the membrane properties in long-term application. Moreover, an increase in the gas flow rate will reduce the gas component residence time results in lower gas absorption rate where increasing the liquid flow rate can prevent liquid saturation by disturbing liquid boundary layer results in higher gas absorption. Therefore, the best gas absorption performance in the hollow fiber membranes can be achieved by controlling the operating parameters at optimum condition.

### 10. Current status and future direction of the technology

Although membrane gas absorption contactors using microporous hollow fiber membranes have attracted great attention in recent years and exciting results have been reported, still most of the researches are at the stage of laboratorial. As mentioned in the previous sections, most of the current researches have focused on the membrane wetting based on membrane characteristics, materials and liquid absorbent properties which can solve the problem of long-term stability in industrial application. Some pilot and full scale membrane contactor installations for gas treatment are in successful operation now. In fact, the long-term reliability of membrane contactors can be proven under industrial conditions.

A large pilot plant gas absorption membrane contactor has been tested by Kvaerner at north of Aberdeen in Scotland for sure natural gas treatment. The membrane contactor is fed with a lean amine stream. The main design parameters of this membrane unit are 88 bar pressure, gas flow rate 5000 Nm<sup>3</sup>/h and liquid flow rate 5 m<sup>3</sup>/h. A novel system developed to keep the pressures on the liquid and vapor sides of the membrane equal. The CO<sub>2</sub> concentration is reduced from an average of approximately 6–3.5% in the gas stream. Another Kvaerner pilot unit is treating flue gas from a gas engine at the Statoil Gas Terminal at Kårstø in Norway. The flue gas rate is 2610 kg/h and 85% of the CO<sub>2</sub> is separated from the gas stream [108]. Currently, the Kvaerner membrane contactor technology is under commercialization. TNO in the Netherlands has also developed a membrane contactor pilot plant for post combustion CO<sub>2</sub> capture that is based on combinations of dedicated absorption liquids (CORAL) with cheap polypropylene membranes. The basic specifications of the pilot plant are gas flow rate 0.5–4 m<sup>3</sup>/h, liquid flow rate 0.5–20 L/h and CO<sub>2</sub> concentration 0.05–10% in the gas stream [17].

An industrial ammonia membrane gas absorption unit for ammonia recovery from off gas stream has been developed in the EU Craft Agate project. The membrane contactor equipped with polypropylene membranes. The product of this unit is ammonium salt solution. The goal of more than 99% ammonia removal efficiencies has been met using the membrane contactor system where the removal efficiency obtained as function of the air flow rate through the membrane gas absorption installation. The capacity of the installation is to recover 83 t/y of ammonia [99].

Therefore, it should be mentioned that although some industrial applications for acid gas capture are available, still a lot of effort should be put in to study the different aspects of the technology to be commercially applicable. In order to fulfill this purpose there are some suggestions which are important to be studied in future researches:

1. Long-term stability of the membrane gas absorption operation is important from an economic point of view. In order to achieve this purpose some criteria such as developing membrane structure and materials (highly porous with small pore size structure, high hydrophobicity, high chemical and thermal stability, good mechanical strength) and developing liquid absorbent properties (non-volatile, high surface tension, high affinity for the acid gas component, chemical compatibility with the membrane material, regenerability) must be considered in future researches.
2. In order to replace conventional gas absorption systems by gas–liquid membrane contactors, not only the technical but also a detail economical analysis of the membrane contactor system for acid gas capture must be taken into consideration. However, it has seldom been considered in the literature.
3. Although, the membrane and liquid absorbent are the most important factors for the acid gas capture, the module configuration can play an important role to improve mass transfer in

gas side and liquid side. Therefore, development of new module for improving mass transfer can be a subject of future research with the important given to features such as the regularity of fibers, packing density and the relative flow directions.

- In order to commercialize the technology, there is need to analysis the acid gas removal based on real gas stream conditions as flue gas or natural gas streams. Simultaneous absorption of different acid gases at high temperature and/or pressure can significantly affect the absorption process in the membrane contactor. However, in most of the previous works either pure acid gas or mixtures with  $N_2$  or  $O_2$  at ambient temperature and low pressure were used as model gas stream in the absorption process.

## 11. Conclusion

Hollow fiber gas–liquid membrane contactor is a new approach used for removal of acid gases from gas streams. This technique combines the advantages of membrane and absorption that offers numerous advantages over gas separation membranes and conventional gas absorption systems. The main researches on hollow fiber gas–liquid membrane contactors were investigated and their main findings were highlighted. Moreover, important aspects such as advantages and disadvantages, current status and future direction of the technology were discussed critically. Hollow fiber gas–liquid membrane contactors with useful characteristics and advantages can compete with gas separation membranes and conventional absorber for acid gas capture. However, much research and development efforts are needed to commercialize the technology.

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