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MEMBRANE WETTING IN CARBON DIOXIDE ABSORPTION PROCESS USING MEMBRANE CONTACTORS: A REVIEW

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Abstract

Porous membranes as gas-liquid contactors are widely used in carbon dioxide (CO₂) absorption systems. It provides larger mass transfer area and excellent operational flexibility. Membrane contactors have been considered as alternative to conventional approaches in removing CO₂. In spite of its advantages over conventional technologies, membrane wetting is a major problem which reduces performance of CO₂ absorption. This paper explains the concept of membrane wetting phenomenon and its influence on the CO₂ mass transfer through the membrane and absorption performance. The factors that cause membrane wetting were presented including hydrophobicity of membranes surfaces, membrane pore size, liquid entry pressure and properties of absorbent liquid. Current proposed methods to alleviate the membrane wetting were reviewed and discussed. Development of mathematical model was presented for all types of membrane wetting modes, as well as its validity for CO₂ physical and chemical absorption.

Key words: CO₂ removal, greenhouse gases, gas absorption, membrane wetting

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1. Introduction

Carbon dioxide has been demonstrated to be the largest component of greenhouse gases that increase the temperature of the earth's surface. About 40% of the CO₂ emissions are produced by the burning of fossil fuels in power plants (Desideri et al., 1999). Conventionally, bubble-column, venture-scrubber, packed-tower and sieve-tray columns are used in the absorption-based of CO₂ capture technology to reduce the CO₂ emission from flue gas (Cozma et al., 2013; Desideri et al., 1999). The gases are randomly dispersed in this equipment to form an interfacial area with a liquid absorbent, which is difficult to estimate. In addition to the problems of flooding, loading, foaming and channelling in conventional absorbers, control of the fluid velocity and the scale-up of these systems are also difficult. An alternative is the membrane contactor system (MCS), which was

developed to overcome these disadvantages. The liquid absorbent usually flows inside the hollow fiber membranes (lumen), while the gas flows at the opposite side (shell) as shown in Fig. 1 and the solvent contacts the gas at the mouths of membrane pores to form stable mass transfer film.

The first technology for gas absorption using hollow fiber membrane was developed by Qi and Cussler (1985a; 1985b), who used sodium hydroxide as a solvent in a hollow fiber membrane contactor. The membrane contactor provides greater gas-liquid contact area, and the overall mass-transfer coefficient is therefore three times greater than that in a packed column using the same solvent (Sea et al., 2002). Moreover, Falk-Pederson and Dannstorm (1997) mentioned that a reduction of greater than 70% in equipment size and 66% in equipment weight can be achieved using a membrane contactor instead of conventional columns.

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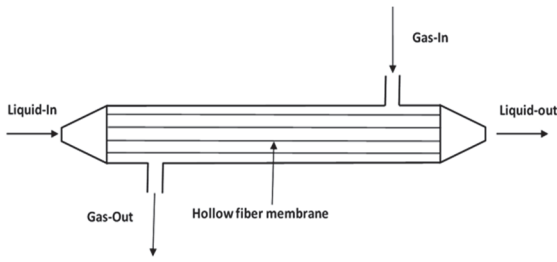


Fig. 1. Parallel flow hollow fiber membrane contactor module

The advantages and disadvantages of membrane contactor have been discussed in more detail by Gabelman and Hwang (1999). In spite of its advantages over conventional technique, membrane wetting represents the main factor which determines the CO₂ absorption rate in membrane gas-liquid contactors.

In this paper, the membrane wetting phenomenon is reviewed. The effect of membrane wetting on the CO₂ absorption performance was presented. The technical development in membrane synthesis and modification to alleviate the membrane wetting was reviewed. Liquid absorbents performance in term of CO₂ absorption rate and its related to the membrane wetting is discussed. Mathematical model development for all operating wetting mode was presented. Furthermore, models validation for physical and chemical CO₂ absorption were reviewed and discussed.

2. Mass transfer in MCS

The CO₂ mass transfer in the porous hollow fiber membrane gas absorption module take place through three stages: (a) diffusion from the bulk gas phase (shell or lumen) to the gas boundary layer on the membrane surface by convective diffusion; (b) diffusion through membrane pores by combining molecular diffusion and Knudsen diffusion; and (c) dissolution (physical and/or chemical) into the absorption liquid at the gas-liquid interphase then diffusion to the liquid boundary layer, eventually to the liquid bulk by convective diffusion. Therefore, three mass transfer resistances will be occurring namely liquid, membrane and gas mass transfer resistance. The overall mass-transfer coefficient **K_{og}** can be expressed in a series-resistance model based on the gas phase (Khaisri et al., 2009) (Eq. 1).

$$1/K_{og} = (1/H_e k_l) + (d_o/k_m d_{ln}) + (d_o/k_g d_i) \quad (1)$$

where: *k_g* is the mass transfer coefficient of gas phase; *k_m* – mass transfer coefficient of membrane; *k_l* – mass transfer coefficient of liquid phase; *d_i* – inner diameters of the fiber; *d_o* – outer diameters of the fiber; *d_{ln}* – logarithmic mean diameters of the fibers; *H_e* – Henry’s constant (dimensionless).

Fig. 2 illustrates the schematic drawing for the overall mass transfer process through the ideal membrane gas absorption system.

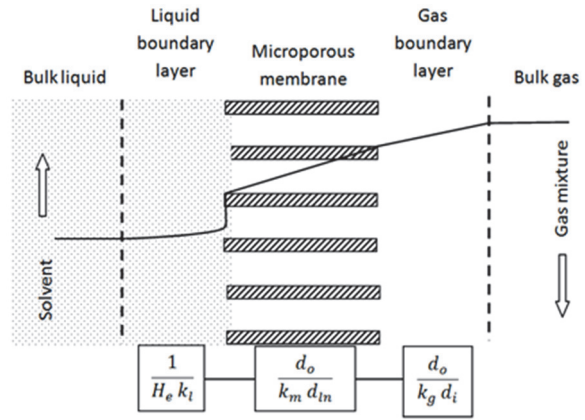


Fig. 2. Schematic drawing of mass transfer regions and resistance-in-series in ideal membrane contactor

3. Membrane wetting property

Principally, membrane wetting is defined as the possibility of the liquid penetrating the membrane pore, which depends on the hydrophobic and hydrophilic properties of the membrane. Therefore, wetting properties can be further classified into three categories (Fig. 3a-c):

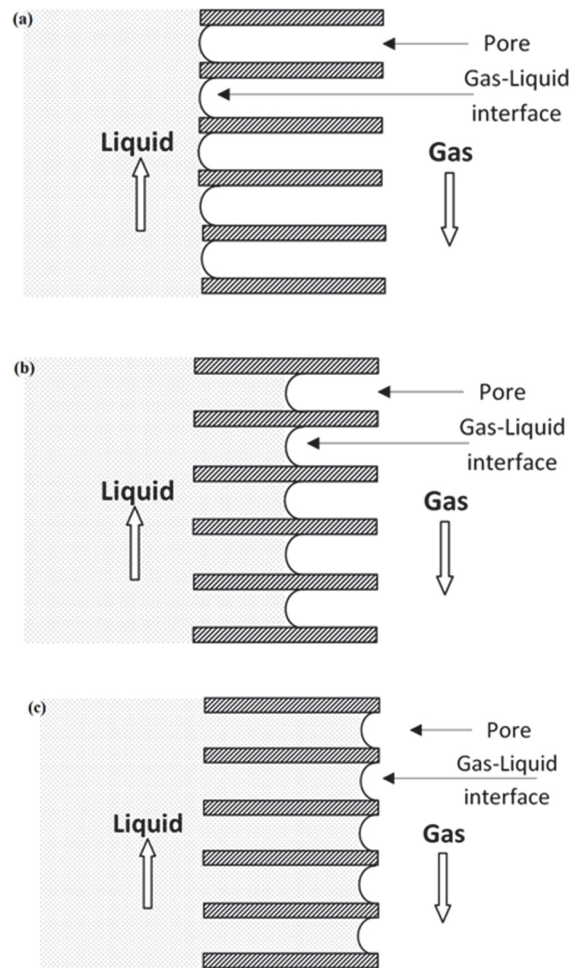


Fig. 3. Pore wetting pattern in hydrophobic microporous membrane: (a) non-wetted; (b) partially wetted; (c) fully-wetted

- a. Non-wetted: The membrane pores are filled with gas, which has minimal membrane resistance to mass transfer, as shown in Figs 3a.
- b. Partially-wetted: The liquid penetrates the pores and partially fills the membrane with liquid, as shown in Figs 3b. A prolonged period of stable operation time will affect its performance because the membrane mass transfer resistance will increase rapidly (deMontigny et al., 2006; Wang et al., 2005). Lv et al. (2010) immersed a polypropylene (PP) fiber in amine solutions for up to 90 days and observed that the membrane was swollen; this swelling reduced the hydrophobicity of the membrane and increased the degree of membrane wettability.
- c. Fully-wetted: In this case, during a prolonged period of operation, the membrane pores completely fill with liquid as presented in Fig. 3c. The presence of stagnant liquid inside the pore leads to the formation of a dead zone, which reduces the overall mass transfer rate.

4. Membrane wetting factors

Many factors are determining the membrane wetting in MCS with long-term of operating. Membrane surface properties in terms of its hydrophobicity, membrane pore size, liquid pressure and absorbent liquid properties have a significant impact on the membrane's wettability.

4.1. Membrane surface hydrophobicity

Membrane surface hydrophobicity has a significant impact on the membrane's wettability. Hydrophobic membranes such as polyvinylidene fluoride (PVDF), (PP) and polytetrafluoroethylene (PTFE) are broadly used in MCS. The PVDF membranes can be fabricated through using phase inversion method, while PP and PTFE membranes can be fabricated by stretching technique that made it more expensive than PVDF membrane. Fig.4. (a-b) illustrate the Scanning Electronic Microscopy (SEM) of the commercial PVDF and PP hollow fiber membranes surface. The PP membrane consists of grooves in the surface structure while PVDF membrane surface has smoothly and relatively uniform structure.

The contact angle (θ) is a factor that characterises the hydrophobicity of the membrane surface. Hydrophilic membrane surfaces exhibit contact angles in the range of $0^\circ < \theta < 90^\circ$, whereas hydrophobic membranes have a θ range of $90^\circ < \theta < 180^\circ$. Therefore, the use of a hydrophobic membrane with a large contact angle could minimise the wetting problem. Commercial PP membranes has high water contact angle with the range of 122° – 127° (Franco et al., 2008; Lv et al., 2012). However, PP membrane surfaces are easily wet when exposed to the absorbent liquid, especially amine solutions (Rangwala, 1996; Wang et al., 2004a) (Fig. 4). Table 1 shows the variation of the contact angle of the PP hollow fiber surface with immersion time into different absorbent liquids. The declination in the surface hydrophobicity

in PP membrane is related to the significant impact of the amine solutions on its surface morphology. The membrane pore structure and dimension change during CO₂ absorption with long-operating period.

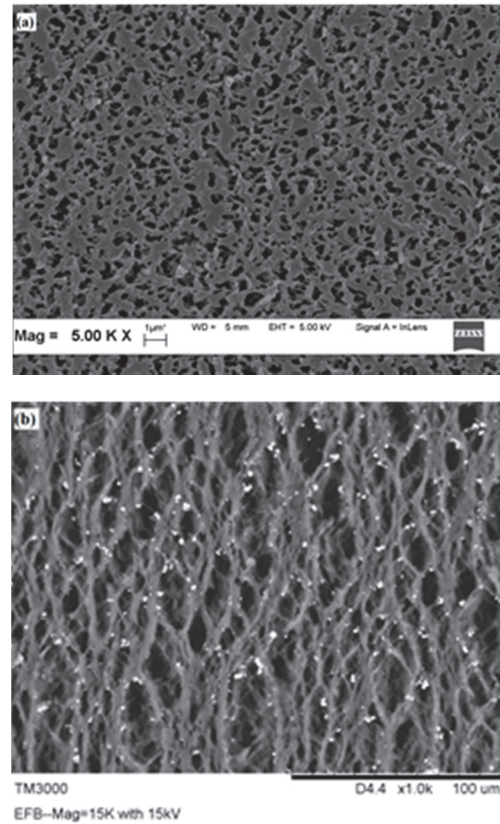


Fig. 4. SEM image for the commercial hollow fiber membrane surfaces: (a) PVDF (Pall Co.); (b) PP (Mycrodyn-Nadir Co.)

Lv et al., 2010 observed that the PP membrane structure changed from slit-like (initial structure) to elliptical or even circular when immersed with MEA aqueous solution for long period of time. However, such DEA amine has less impact on PP membrane surface morphology than MEA (Figs. 5-6) thus the possibility of membrane to wet could be less.

An experimental study for CO₂ absorption in PP membrane contractor over three months was carried out by Wang et al. (2005) using 2 M DEA aqueous solution as absorbent. It was revealed that the CO₂ flux reduced about 20% at the initial stage of 4 days of operation and then there is no change in the performance.

Table 1. Variation of contact angle on PP membrane surface with immersion time for deionized water, 30 wt.% monethanolamine (MEA) and 30 wt.% methyl-diethanolamine (MDEA) (Lv et al., 2010)

Time (day)	Contact angle (degree)		
	Deionized water	30 wt.% MEA	30 wt.% MDEA
0	121.6	121.6	121.6
20	108	105	104
40	104	101.5	97.8
60	99.7	93.6	90.8

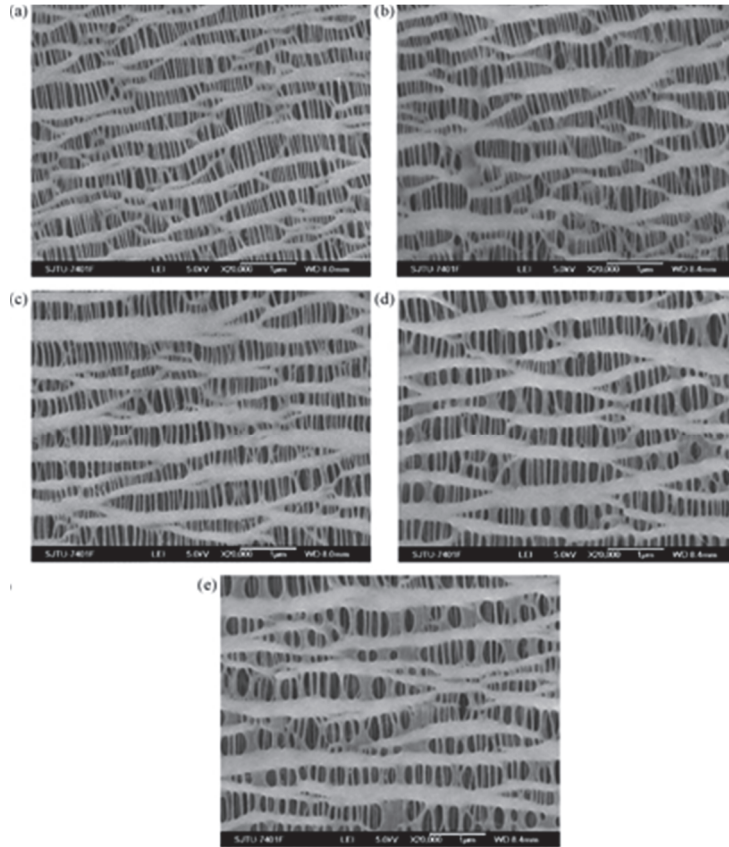


Fig. 5. SEM image for PP membrane surface (a) non-immersed PP fibers; PP fibers immersed in 30 wt.% MEA for: (b) 10 days, (c) 30 days, (d) 60 days, (e) 90 days (Lv et al., 2010)

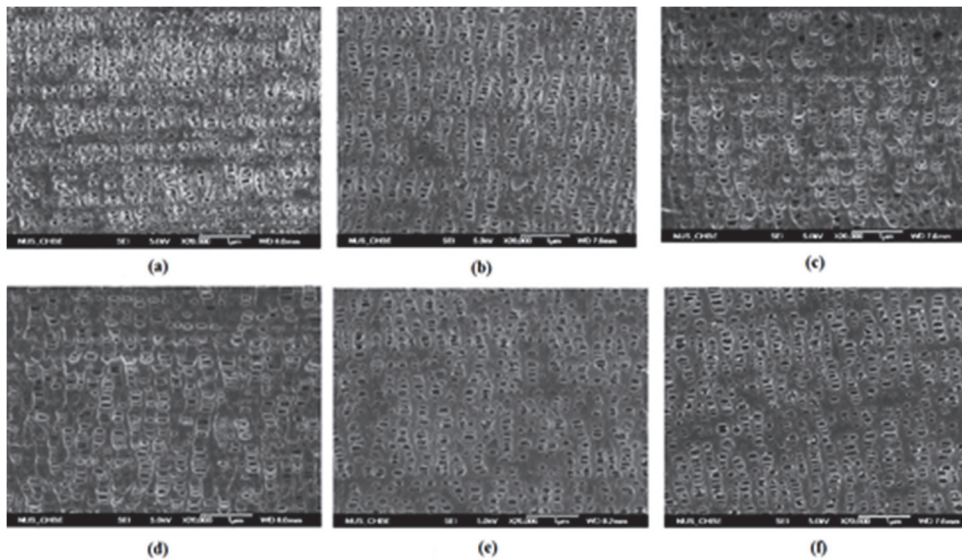


Fig. 6. SEM image for PP membrane surface (a) non-immersed PP fibers; PP fibers immersed in 2 M DEA for (b) 2 days, (c) 4 days, (d) 10 days, (e) 20 days, (f) 30 days (Wang et al., 2005)

PTFE membranes inherently chemical resistance. Consequently, it was suggested the best membrane gas-liquid contactors for CO₂ absorption using absorbent of amine solutions (Matsumoto et al., 1994; Nishikawa et al., 1995; Falk-Pedersen and Dannstrom, 1997). Fig. 7 demonstrates the performance of PP and PTFE hollow fiber membrane contactors used for CO₂ absorption with

monoethanolamine solution (MEA) as absorbent. As shown, PP membrane suffer from significant surface wetting under long time of operating period which leads to decrease overall volumetric gas-phase mass transfer coefficient ($K_G a$). In contrast, PTFE membrane exhibit insignificant declination in $K_G a$ even used it for a long period of time of CO₂ absorption period.

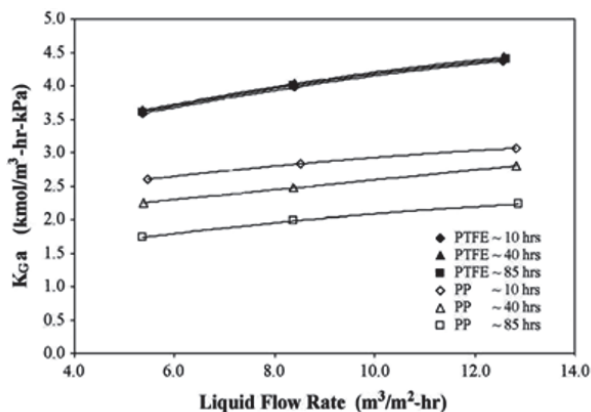


Fig. 7. Effect of operating time on PP and PTFE membrane performance for CO₂ using MEA of 2 M (deMontigny, et al., 2006)

4.2. Critical liquid entry pressure

The liquid pressure is an additional factor which significantly affects the membrane wetting, where the increased in liquid pressure leads to an increasing possibility of liquid penetration through the membrane pores. Almost all absorbents performance are dependent on the CO₂ partial pressure. However, the increasing pressure in the gas phase leads to the formation of gas bubbles in the liquid phase; resulting non-uniform gas-liquid interface. Li and Teo (1996) fabricated polyethersulfone hollow fiber membrane with thin dense layer to reduce the membrane wetting rate in the CO₂ absorption system under high pressure condition.

It was observed that the CO₂ absorption flux was low due to the increasing of the membrane resistance. The minimum pressure at which the liquid penetrates the pores is called the critical entry pressure (ΔP_c). It can be estimated using the Laplace equation (Franken et al., 1987; Kumar et al., 2002) (Eq. 2):

$$\Delta P_c = 2\gamma_L \cos\theta / r_{pm} \quad (2)$$

where: γ_L - the liquid surface tension; r_{pm} - maximum radius of the membrane pores.

The critical pressure can be measured experimentally by gradually increasing the pressure of the liquid applied on the membrane and observing the first liquid droplet on the outer surface of the membrane (Mansourizadeh and Ismail, 2011a). In order to limit the membrane wetting effect, the operating pressure should be less than the critical pressure. Fig. 8 shows the variation of ΔP_c with ethanol content in distilled water for PP and PTFE membranes.

It can be observed that PTFE membrane has ΔP_c higher than PP membrane at same the ethanol content due to its high surface hydrophobicity property compared to PP as aforementioned. The initial parts of the membranes in the hollow fiber membrane modules can be wetted gradually during long-term operation with the application of high liquid pressure (Kumar et al., 2002; Sea et al., 2002).

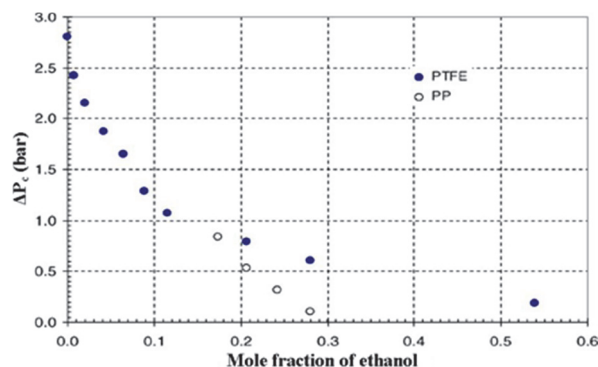


Fig. 8. Critical entry pressure for aqueous ethanol solutions in PP and PTFE membranes (Dindore, et al., 2004)

4.3. Membrane pore size

The pore size of membrane plays a significant role in membrane wetting during gas-liquid contact. The relation between the pore size and ΔP_c was inversed relationship (Eq. 2). Consequently, smaller membrane pores size decreases the likelihood of membrane wetting, whereas larger pores diameter result in a fast rate of membrane wetting at same membrane material type and liquid properties in contact with its surface (Chen et al., 2010; Lu et al., 2008). Membranes with small pore size and relatively low surface hydrophobicity was found to have high membrane wetting resistance compared to membranes of high surface hydrophobicity but large pores size (Mansourizadeh and Ismail, 2011b). Sea et al., (2002) investigated CO₂ absorption performance in PVDF, PTFE and PP hollow fiber membranes with pore size of 0.03, 1 and 0.25 μm , respectively, using MEA as absorbent liquid. According to Sea et al., (2002), it was observed that the smallest pore size membrane (PVDF) has higher CO₂ absorption flux than others although their surface hydrophobicity is higher than PVDF membrane.

Mansourizadeh and Ismail (2011b) prepared PVDF hollow fiber membrane with pore size of 3.96 nm via phase inversion method. The membrane tested in CO₂ absorption system and compared with results reported by Xu et al. (2008) for CO₂ absorption in commercial PTFE hollow fiber membrane (1 μm pore size) at the same operating conditions. The results exhibited high CO₂ absorption for PVDF membrane compared to commercial PTFE membrane. Moreover, the prepared PVDF membrane lost approximately 25% of the initial flux after 26 hr of operating and maintained the rest flux until the end of the operation (140 hr).

4.4. Absorbent liquid properties

The membranes used in gas absorption are not selective; the CO₂ selectivity is dominated by the absorbent liquid. A large amount of experimental data has been reported for CO₂ absorption system using different solvents, including either physical or chemical absorption. The absorption liquid surface

tension property plays an important role in determining the efficiency of the membrane gas-absorption process. According to the (Eq. 2), the surface tension of an absorbent liquid that is used as the CO₂ absorbent liquid should be sufficiently high to limit membrane wettability during long-term operation. The desirable features of the solvent liquid include a high reactivity with CO₂, a high loading capacity, a surface tension value that is asymptotic to the water or higher, a low regeneration cost, a lack of volatility, good chemical stability and low toxicity. The conventional absorbent liquids are alkanolamine solutions, such as those of MEA, 2-amino-2-methyl-1-propanol (AMP), diethanolamine (DEA) and MDEA. The chemical reaction rate is directly proportional to any increase in the amine concentration. Initially, this relationship appears to be a useful way to increase the CO₂ absorption flux in a MCS. Unfortunately, the surface tension of amine solutions decreases when high concentrations of amines are applied, as shown in Table (2).

Table 2. The surface tension for alkanolamine + water solutions at 25 °C

Alkanolamine	Reference	Concentration (mass fraction)	Surface tension (mN m ⁻¹)
MEA	Vazquez et al. (1997)	0.000	72.01
		0.015	68.45
		0.112	60.41
		0.307	55.99
AMP	Vazquez et al. (1997)	0.011	59.74
		0.119	41.22
		0.320	37.00
DEA	Vazquez et al. (1996)	0.019	66.70
		0.102	58.82
		0.285	54.32

The drop-in surface tension value leads to an increased possibility of solvent penetration into the pores of the membrane during long operating periods. Fig. 9 shows the effect of MEA concentrations on CO₂ flux throughout 12 days of operation. It can be observed that the CO₂ flux declining increases with the increasing of MEA concentration. Faiz and Al-Marzouqi (2010) performed a theoretical investigation on a hydrophobic membrane contactor using water and MEA as the absorption liquids. The results indicated that an increased concentration of MEA enhanced the CO₂ removal with a concomitant increased in the wetting rate (Faiz and Al-Marzouqi, 2010). Consequently, the concentration of organic material should not exceed the maximum allowable value to avoid membrane wettability.

Lu et al., (2008) pointed out that organic solutions used as absorbents for CO₂ are broadly resulting in the liquid penetrating of membrane pores more easily than water. Fig. 10 illustrates the CO₂ absorption flux behaviour during 12 days of operation for absorbents of deionized water and 1M aqueous solutions of MEA, DEA, and AMP in commercial PVDF hollow fiber membrane contactor. Unlike the case of deionized water, the CO₂ flux decreased with

the operating time when aqueous amines solutions were applied as absorbents.

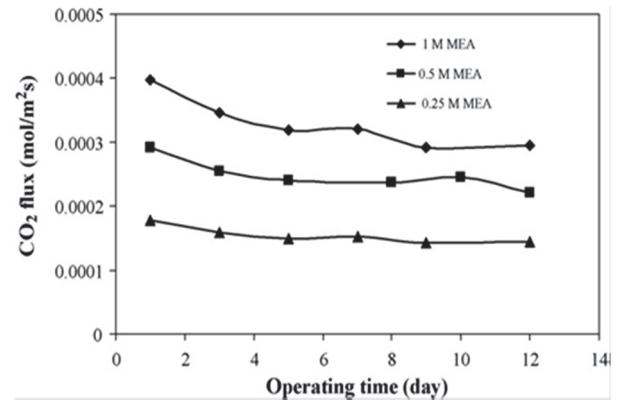


Fig. 9. Effect of amine concentration on long-term performance of hollow fiber membrane contactor (Rongwong et al., 2009)

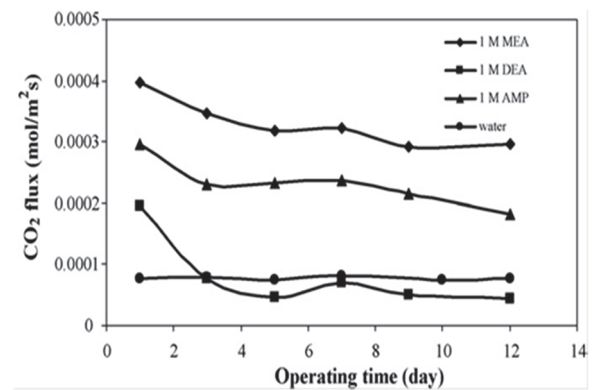


Fig. 10. Effect absorbent type on long-term performance of hollow fiber membrane contactor (Rongwong et al., 2009)

5. Membrane wetting reduction methods

Recently, many research efforts have been aimed at enhancing the CO₂ absorption performance by reducing the membrane wettability when using membrane as gas-liquid contactor. Many researchers have focused on non-solvent additives in the membrane synthesis steps to control the membrane structure and pores size. Others have changed the surface morphology to increase the membrane surface hydrophobicity. In addition, a plasma treatment was conducted to functionalise the membranes surface according to the treatment medium, such as CF₂, CF₄.

5.1. Membrane synthesis and additives

The flux of CO₂ is strongly related to the effective surface porosity of hydrophobic membranes when they are used as gas-liquid contactors. One of the important factors that dominating the membrane porosity during the manufacturing process is the polymer concentration. Bakeri et al. (2010) mentioned that the permeance, mean pore size and effective surface porosity of polyetherimide (PEI) hollow fiber membranes were decreased when the polymer

concentration in the dope solution was gradually increased from 10 to 15 wt. %, as shown in Table (3).

Table 3. Effect of polymer concentration for fabrication of PEI hollow fiber membranes property (Bakeri et al., 2010)

Polymer concentration (Wt.%)	Mean pore size (nm)	Effective surface porosity (m^{-1})
10	9.3	95,596
11	8.9	21,126
12	7.1	14,964
13	4.8	10,714
14	4.4	2113
15	3.9	1932

Numerous investigations have been conducted to enhance the structures of membranes by using non-solvent additives to control the precipitation rate of the polymer dopes used in the phase-inversion method to enhance the surface properties. Polyethylene glycol 300, glycerol, ethanol and acetic acid were used by Mansourizadeh and Ismail (2010a) as non-solvent additives in the spinning dope to fabricate polysulfone (PSF) hollow fiber membranes. They similarly applied glycerol, phosphoric acid, ethanol and polyethylene glycol (PEG-400) to produce PVDF hollow fiber membranes (Mansourizadeh and Ismail, 2011a). It was pointed out that, among the additives used in both works, glycerol provided a larger pore size and greater surface porosity. The authors attributed these result to the high precipitation rate; thus, the CO₂ absorption flux was 30% higher than that observed in the plain membrane in the case of PVDF.

In addition, a high degree of tortuosity was achieved due to the membrane's sponge-like structure; as a consequence, the absorbent cannot easily penetrate the membrane pores and wet the membrane. For comparison, the PVDF membrane exhibited greater permeability due to the pore size and porosity being greater than that of PSF when glycerol was used as a non-solvent additive (Ismail and Mansourizadeh, 2010). In another work, the authors added lithium chloride (LiCl) at different concentrations to the PVDF membrane dope solution (Mansourizadeh and Ismail, 2010b). The PVDF hollow fiber membrane produced exhibited a CO₂ absorption flux approximately 60% higher than that of a plane PVDF membrane when 2 wt.% LiCl was added to the spinning dope as a non-solvent additive. In addition, a PVDF hollow fiber membrane with a large mean pore size, which was prepared using orthophosphoric acid as the non-solvent, exhibited a CO₂ flux 33% greater than that observed in a membrane with a high surface porosity that was prepared using lithium chloride monohydrate (LiCl·H₂O) (Mansourizadeh et al., 2010). The diffusion coefficient is appreciably higher in the larger pores of membranes than in the smaller pores; therefore, the benefits of higher surface porosity are limited by the effects of the small pore size on the CO₂ flux. From the previous investigations the authors aimed to produce membranes with larger pore, high porosity and spongy cross section structure.

Membrane of large pore size could easily wet at low critical pressure (Eq. 2) as well as the finger-like structure increases the possibility of the membrane wetting. The authors referred to sponge structure of the PSF and PVDF membrane; however, the effect of the hybrid sponge-like and finger-like structure were neglected as shown in Fig. 11a-c.

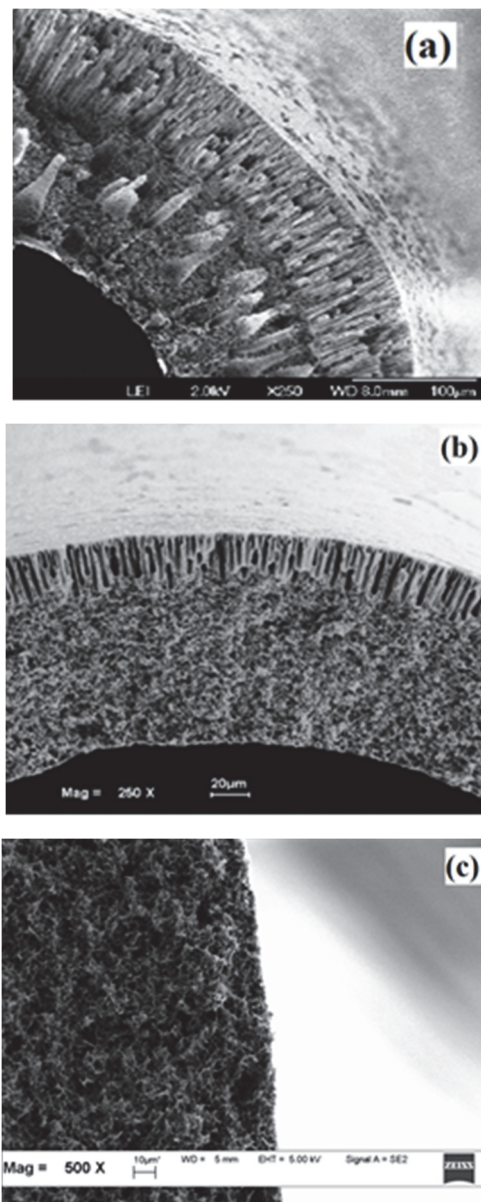


Fig. 11. SEM image for Cross-sectional morphology of the membranes (a) PSF with glycerol (Mansourizadeh and Ismail, 2010a); (b) PVDF with glycerol (Mansourizadeh and Ismail, 2011a); (c) commercial PVDF (Pall co.)

More investigation is required to observe the impact of the hybrid structure of obtained membranes on the CO₂ absorption performance with long operating period of time. Fig. 12 illustrates SEM of the alone sponge-like structure of the commercial (Pall co.) microporous PVDF membrane.

Another interesting research on PVDF hollow fiber membrane was fabricated by [Rahbari-Sisakht et al.](#) (2012) using surface modifying macromolecule as

additives in the spinning dope. It was revealed that the modified membrane has higher CO₂ absorption compared to PVDF membranes without additives. Moreover, the modified membrane maintained about 92.3% of the CO₂ absorption flux during 150 hrs of operating. However, the stability study was conducted via distilled water. Therefore, more investigation is required to exhibit the stability of membrane via conventional absorbent such as MEA and MDEA.

5.2. Treatment of membrane surface

The membrane surface hydrophobicity can be enhanced via fabrication of a superhydrophobic surface which is in contact with liquid absorbent. This target was successfully achieved through the generation of a polymeric rough surface or fluorination of polymeric membrane surface using plasma.

5.2.1. Membrane of rough surface

High water contact angle (WCA) surfaces with self-cleaning property are naturally available such as the leaves of the lotus plant (Barthlott and Neinhuis, 1997), leaves of Indian cress and wings of butterflies (Neinhuis and Barthott, 1997; Wagner et al., 1996). This natural phenomenon may be attributable to the lotus like structure, which composes of nano- and micro-structures. Thus, the research community has dedicated serious attentions to explore the fabrication of polymeric surfaces that are closed to the natural morphologies.

Recently, a simple and inexpensive technique was proposed to create superhydrophobic surface via a solvent- non- solvent additives coating method (Chen et al., 2009; Erbil et al., 2003; Li et al., 2006; Lu et al., 2004). This method induces the polymeric surfaces to form the lotus-like structure. The fundamental concept of this technique is the ability of non-solvent to aggregate the nano- and micro-scale aggregations on the coated surface which is responsible to increase the surface roughness thus enhances its hydrophobicity. Various types of non-solvent additives with different boiling point were used in this technique to fabricate superhydrophobic polymeric surfaces. Erbil et al. (2003) obtained gel-like porous surface of PP that had WCA of 160° using p-xylene and Methyl ethyl ketone (MEK) as solvent and non-solvent, respectively. Consequently, high contact angle of rough surfaces were produced to reduce the membrane wetting in CO₂ absorption system.

The WCA of the coated PP flat-sheet membrane using cyclohexanone as non-solvent additive in xylene/polypropylene solution was 169°, which is 42° higher than that was observed for the untreated membrane and 30° higher than PTFE membrane (Franco et al., 2008). Fig. 12 (a-b) demonstrate the structure of PP rough surface and their nano- and micro- structure which responsible for the surface roughness, respectively. Recently, Lv et al. (2012) used a mixture of cyclohexanone and MEK as

a non-solvent to fabricate a superhydrophobic layer on a PP hollow fiber membrane.

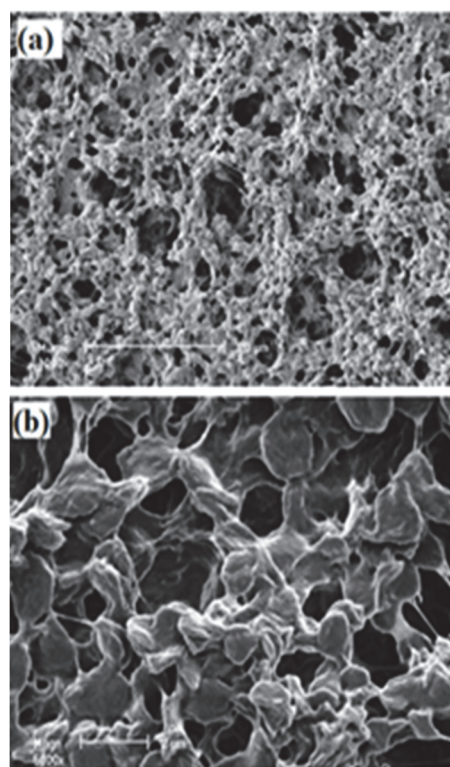


Fig. 12. SEM image for (a) PP rough surface; (b) high magnification of (a) (Franco et al., 2008)

It was observed that the surface WCA increased dramatically from 122° to 158°. The pristine and superhydrophobic PP membranes were tested in continuous CO₂ absorption system for 20 days using 1M MEA as absorbent. Superhydrophobic membrane maintained approximately 86% of the initial CO₂ absorption flux. In contrast, the pristine PP membrane suffered from membrane wetting wherein it was lose 79% of the initial flux at the end of operating time.

Despite of these advantages that could reduce the membrane wetting, the superhydrophobic layer leads to an increased in the mass-transfer resistance due to an increased in the membrane thickness. Therefore, the optimization of the resistance of the additional layers on a treated membrane to the resistance of the liquid that passes through the untreated membrane pores with prolonged operating time is important.

5.2.2. Plasma treatment

Plasma treatment technique is superior to other treatment methods. This technique can produce either a hydrophilic surface on the membrane with a low WCA with high water permeability (Jaleh et al., 2010) or a hydrophobic membrane with a high WCA (Bae et al., 2001; Lin et al., 2009a, 2009b). Treatment of PP hollow fiber membrane with CF₄ in a plasma reactor increases its surface of WCA from 117° to 143° (Lin et al., 2009a). In addition, the CO₂ flux in treated membrane was 8% higher than untreated membrane

using 1M 2-amino-2-methyl-1-propanol (AMP) as absorbent. Using the same method, Lin et al. (2009b) achieved a WCA of 155° on a treated flat-sheet PVDF membrane surface, which was 23° higher than WCA for an untreated membrane. It was also observed that the CO₂ absorption fluxes increased to 7% and 17% over the plane PVDF and PTFE, respectively, when 1M AMP was used as the absorbent. The improvement in membrane hydrophobicity is related to the increased of the elemental fluorine-to-carbon ratio (F/C), which reduces the membrane surface energy. The increasing in treatment time has insignificant effect in PVDF than PP as shown in Table 4. This is because the PVDF membrane surface became saturated with fluorine bonds at short treatment time.

Table 4. Effect of plasma treatment on the membrane surface characteristics

PVDF flat sheet (Lin et al., 2009b)			PP hollow fiber (Lin et al., 2009a)		
Time (min)	WCA (°)	F/C	Time (min)	WCA (°)	F/C
0	133	0.88	0	115	0
1	153	1.25	1	126.8	0.77
2.5	153.4	1.52	2	135	0.94
5	155	1.6	3	139	0.98
7.5	155	1.68	4	141.5	1.06
10	155	1.68	5	142.9	1.13
			6	143	1.12

Using plasma in membrane surface treatment could lead to the increasing of the surface roughness due to etching by plasma (Lin et al., 2009a). Consequently, there are two reasons being for the increasing of membrane surface when applying plasma: reducing the surface energy and increasing the surface roughness. Fig. 13 a-b demonstrate the surfaces of non-treated PP membrane with roughness value of 53.02 and plasma-treated PP membrane with roughness value of 58.22.

The orange colour in Fig. 13b represents the initial top surface of treated PP membrane with plasma. The limitations of the application of plasma treatment are the construction of the required equipment in industrial facilities, the toxic properties of the fluorine gases and the high costs.

5.3. Liquid absorbent developments

The development of a new absorption liquid to meet the successful of CO₂ absorption requirements in membrane contactor, which include surface tensions greater than water and compatibility with polyolefin, is crucial. Many works have been conducted using a mixture of alkanolamines to enhance the reaction rate and physical properties of the absorbent liquid (Gong et al., 2006; Paul et al., 2008; Rongwong et al., 2009). Aqueous solutions of amino acid salts have been used as alternative absorbent liquids due to its high surface tension values (higher than water), and it has CO₂ same absorption properties as alkanolamines (Feron et al., 1995; Kumar et al., 2002).

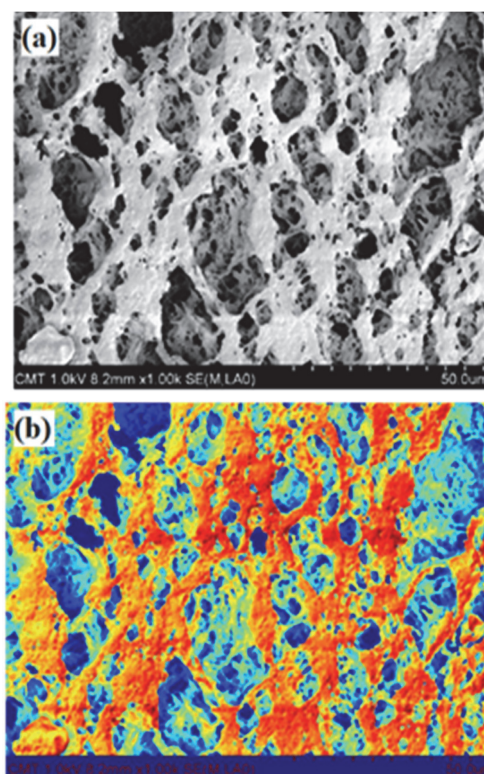


Fig. 13. SEM image for PP surface: (a) non-treated; (b) plasma-treated (Lin et al., 2009a)

Yan et al. (2007) pointed out that the surface tension of a potassium glycinate (PG) solution is proportional to the increased in solvent concentration. Table 5 shows the surface tension and ΔP_c for CO₂ loaded and unloaded aqueous solutions of MEA and potassium salt of taurine (PST) at 295 K in PTFE membrane.

Table 5. Surface tension and ΔP_c for loaded and unloaded CO₂ absorbents at 295 K (Kumar et al., 2002)

CO ₂ absorbent	CO ₂ loading (wt %) (mol CO ₂ /mol amine)	Surface tension (mN m ⁻¹)	ΔP _c (kPa)
water	Unloaded	72.3	25.4
2M MEA	Unloaded	68.2	18.2
2M MEA	0.05	69.1	23.0
2M MEA	0.12	70.2	—
2M MEA	0.28	72.6	25.5
1M PST	Unloaded	72.9	25.4
2M PST	Unloaded	74.4	25.9
4M PST	Unloaded	77.5	—
2M PST	0.04	74.8	27.7
2M PST	0.17	75.3	—
2M PST	0.32	76.1	—

In recent years, piperazine has been proposed as efficient absorbents in terms high of CO₂ absorption rate and high surface tension and viscosity values compared to amine solutions (Bishnoi and Rochelle, 2000; Derks et al., 2005; Dugas and Rochelle, 2009; Rochelle et al., 2011). Piperazine even adopted as a prompter to enhance alkanolamine solutions reactivity

with CO₂ and its surface tensions (Lu et al., 2007). Lin et al. (2009a) applied CO₂ absorbents of AMP, PZ and its mixtures in PP and PVDF hollow fiber membrane contactors. It was observed that the absorption flux increased from 0.00018 kmol/m³·s using 1M AMP to 0.0024 kmol/m³·s when 0.1 M PZ was added to 1M AMP.

The experimental results of Yeon et al. (2004) indicated that the absorption rate of a PZ and triethanolamine (TEM) mixture is higher than that of TEA alone by a factor of approximately eight; the authors attributed this result to the high reaction rate of PZ with CO₂. An increased of the PZ concentration clearly increased the surface tension of the alkanolamines solutions, as shown in Table 6, which reduces the membrane wetting during prolonged operation.

Table 6. Surface tension of aqueous solution of PZ/H₂O, PZ/AMP/H₂O at 25 °C (Murshid et al, 2011)

Piperazine (wt %)	AMP (wt %)	Water (wt %)	Surface tension (mN m ⁻¹)
1.74	0	98.26	70.97
3.45	0	96.55	69.95
10.35	0	89.65	69.41
1.74	28.26	70	45.39
3.45	26.55	70	46.02
10.35	19.65	70	47.83

6. Mathematical model development

Investigations of the performance of hollow fiber membrane contactors for CO₂ transport had been performed by numerous researchers, and a comprehensive two-dimensional mathematical model had been developed. Almost all of the models had been based on hollow fiber modules under the assumptions that the liquid flows inside the hollow fibers (lumen), while the gas flows in the shell side in a parallel configuration (Al-Marzouqi et al., 2008a; Faiz and Al-Marzouqi, 2010; Sohrabi et al., 2011). The advantage of this arrangement is that the dimensions of the lumen channels can be easily defined and numerical solutions could therefore be easily obtained. Fig. 14 illustrates the schematic diagram for a hollow fiber membrane and model domain. The following assumptions had been considered in development of mathematical model:

- steady-state and isothermal conditions;
- a fully developed laminar parabolic velocity profile inside the hollow fiber (lumen);
- ideal gas behaviour and laminar gas flow imposed in the shell side;
- Henry's law is applicable for the gas-liquid interface

6.1. Shell-side equations

According to Fick's law of diffusion, the diffusion flux can be estimated, and the continuity equation for CO₂ in the shell-side of membrane contactor can be written as Eq. (3):

$$D_{g,s} [(\partial^2 C_{g,s} / \partial r^2) + (1/r)(\partial C_{g,s} / \partial r) + (\partial^2 C_{g,s} / \partial z^2)] = u_{z,s} (\partial C_{g,s} / \partial z) \quad (3)$$

where: $D_{g,s}$ is the diffusion coefficient of CO₂ gas in the shell-side; $C_{g,s}$ – CO₂ concentration in the shell-side; $u_{z,s}$ – the shell-side velocity.

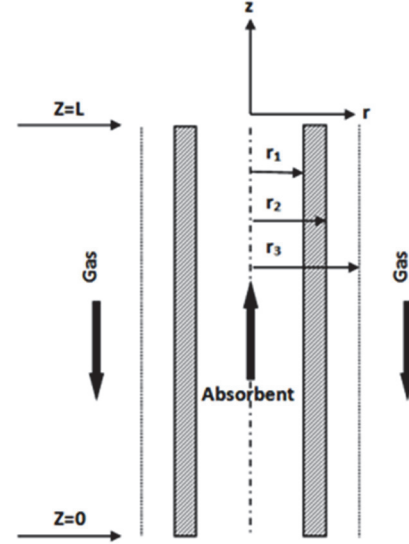


Fig. 14. Schematic diagram for a hollow fiber membrane and model domain

Usually, Happel's model employed in order to characterize the shell-side velocity in laminar flow as Eq. (4) (Happel, 1959):

$$u_{z,s} = 2 u_{av,s} [1 - (r_2/r_3)^2] [((r/r_3)^2 - (r_2/r_3)^2 + \ln(r_2/r)) / (3 + (r_2/r_3)^4 - 4(r_2/r_3)^2 + 4\ln(r_2/r_3))] \quad (4)$$

where: $u_{av,s}$ is the average velocity in the shell side; r_2 – outer radius of the fibers; r_3 – radius of the free surface (Fig. 13), which can be defined as Eq. (5):

$$r_3 = r_2 (1 / (1 - \Phi)) \quad (5)$$

where: Φ is the module void volume fraction that can be determined as:

$$1 - \Phi = (N r_2^2 / R_s^2) \quad (6)$$

where: N is the number of hollow fibers in the module; R_s – inner radius of the module.

The boundary conditions can be employed for (Eq. 3) according to the membrane wetting operating mode as Eqs. (7-9):

(i) *Non-wetted mode*

$$z=L, C_{g,s} = C_{g,s}^o \text{ (inlet conditions)} \quad (7)$$

$$r = r_3, (\partial C_{g,s} / \partial r) = 0 \text{ (symmetry condition)} \quad (8)$$

$$r = r_2, C_{g,s} = C_{g,m} \quad (9)$$

where: $C_{g,m}$ is the CO₂ concentration on the membrane-side.

(ii) Partially-wetted mode

Boundary conditions for non-wetted mode are applicable for (Eq. 3) in case of partially-wetted mode.

(iii) Fully-wetted mode

In this case, considering Eqs. (7, 8), the liquid fills the membrane pores and the boundary condition for continuity equation for CO₂ in the shell-side of membrane contactor can be written as Eq. (10):

$$r = r_2, C_{g,s} = C_{g,m}^* / m_g \quad (10)$$

where: $C_{g,m}^*$ is the CO₂ concentration in the liquid-filled membrane pores; m_g – solubility of CO₂ in the absorbent liquid.

6.2. Membrane-side equations

To express the equations for CO₂ transport through the membrane, the type of wetted mode had been considered. Fig. 15 illustrates the schematic diagram of the partially-wetted mode of membrane in gas absorption system.

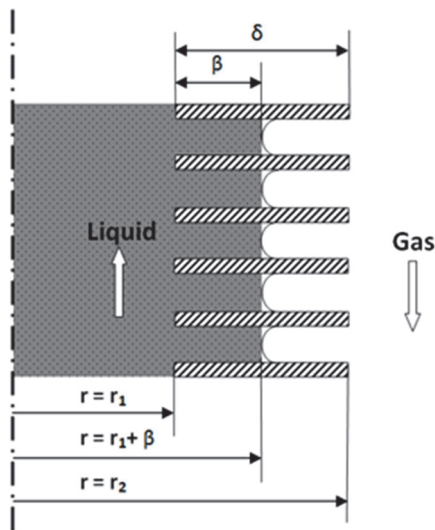


Fig. 15. Schematic diagram for the membrane of partial wetting mode in the gas absorption process

The absorbent liquid flows in the lumen side while the gas flows counter currently in the shell-side. When the length of liquid penetrates membrane pores (β) equals to zero, the membrane operates at non-wetted mode. While, if β equals the membrane's thickness (δ), the membrane at fully-wetted operating mode. The following assumptions can be taken into consideration:

- no convective flux of CO₂;
- the CO₂ transport inside the membrane is due to molecular diffusion;
- the diameter of the pore is uniform.

The steady-state continuity equation for CO₂ transport in membrane contactor can be written according operating of membrane wetting mode as:

I. Non-wetted mode

In this mode, the gas only fills the pores of the membrane and the mass transfer resistance of the filled-gas is assumed negligible. The steady-state continuity equation for CO₂ transport in membrane-side formulated as Eq. (11):

$$D_{g,m} [(\partial^2 C_{g,m} / \partial r^2) + (1/r)(\partial C_{g,m} / \partial r) + (\partial^2 C_{g,m} / \partial z^2)] = 0 \quad (11)$$

where: $D_{g,m}$ is the diffusion coefficient of CO₂ in the membrane-side which can be defined as Eq. (12) (Wang et al., 2004a):

$$D_{g,m} = (D_{g,s} \epsilon) / \tau \quad (12)$$

where: ϵ is the membrane porosity; τ – tortuosity of the membrane pore.

The boundary conditions for (Eq. 11) at non-wetted mode are Eqs. (13-14):

$$r = r_2, C_{g,m} = C_{g,s} \quad (13)$$

$$r = r_1, C_{g,m} = C_{g,t} / m_g \quad (14)$$

where: $C_{g,t}$ is the CO₂ concentration in the tube-side (lumen) of membrane.

II. Partially-wetted mode

In this mode, an additional mass transfer resistance will occur due to presence of liquid in the membrane pores. One portion of the membrane will be filled with liquid while the other portion with gas (Fig. 16). According to this arrangement, the boundary conditions for (Eq. 6) at non-wetted can be written as follows:

III. Gas portion in membrane

(Eq. 12) is applicable for the filled- gas portion of membrane with the following boundary conditions (Eq. 15):

$$r = r_1 + \beta, C_{g,m} = C_{g,m}^* / m_g \quad (15)$$

$$r = r_2, C_{g,m} = C_{g,s} \text{ (Eq. 13)}$$

IV. Liquid portion in membrane

The transport of CO₂ through the liquid-filled portion of membrane takes place due to the molecular diffusion and chemical reaction with absorbent liquid. The concentration equation for CO₂ and absorbent in this portion can be formulated as Eqs. (16-17)(Zhang et al., 2008):

$$D_{g,m}^* [(\partial^2 C_{g,m}^* / \partial r^2) + (1/r)(\partial C_{g,m}^* / \partial r) + (\partial^2 C_{g,m}^* / \partial z^2)] = r_g \quad (16)$$

$$D_{l,m} [(\partial^2 C_{l,m} / \partial r^2) + (1/r)(\partial C_{l,m} / \partial r) + (\partial^2 C_{l,m} / \partial z^2)] = r_l \quad (17)$$

where: $D_{g,m}^*$ is the CO₂ diffusivity in the liquid phase in the membrane-side; $D_{l,m}$ – absorbent diffusivity in the liquid phase inside the membrane pore; r_g –

reaction rate of CO₂ with absorbent in liquid phase; r_l – reaction rate of absorbent in liquid phase.

$D_{g,m}^*$ and $D_{l,m}$ can be defined by Eqs. (18-19) (Zhang et al., 2008):

$$D_{g,m}^* = (D_{g,t} \varepsilon) / \tau \quad (18)$$

$$D_{l,m} = (D_{l,t} \varepsilon) / \tau \quad (19)$$

where: $D_{g,t}$ is the diffusion coefficient of CO₂ in the tube-side of membrane; $D_{l,t}$ – diffusion coefficient of absorbent liquid in the tube-side of membrane.

The boundary conditions for Eqs (16-17) can be written as Eqs. (20-21):

$$r = r_1 + \beta, C_{g,m}^* = C_{g,m} m_g \quad (20)$$

$$r = r_1 + \beta, (\partial C_{l,m} / \partial r) = 0 \quad (21)$$

$$r = r_1, D_{g,m}^* (\partial C_{g,m}^* / \partial r) = D_{g,t} (\partial C_{g,t} / \partial r) \quad (22)$$

$$r = r_1, D_{l,m} (\partial C_{l,m} / \partial r) = D_{l,t} (\partial C_{l,t} / \partial r) \quad (23)$$

where:

$C_{l,t}$ is liquid absorbent concentration in the tube-side of membrane.

V. Fully-wetted mode

In this operating mode, the absorbent fills membrane pores and therefore $\beta = \delta$. Eqs. (16-17) are applicable to formulate concentration equation for CO₂ and absorbent at fully-wetted mode with the following boundary conditions (Eqs. 22-25):

$$r = r_1, D_{g,m}^* (\partial C_{g,m}^* / \partial r) = D_{g,t} (\partial C_{g,t} / \partial r) \quad (\text{Eq. 22})$$

$$r = r_1, D_{l,m} (\partial C_{l,m} / \partial r) = D_{l,t} (\partial C_{l,t} / \partial r) \quad (23)$$

$$r = r_2, C_{g,m}^* = C_{g,s} m_g \quad (24)$$

$$r = r_2, (\partial C_{l,m} / \partial r) = 0 \quad (25)$$

6.3. Tube-side equations

The solvent flow inside a hollow fiber has been assumed to Newtonian laminar flow. The carbon dioxide is absorbed and reacted with the solvent; therefore, the continuity equations for CO₂ and solvent concentration can be expressed as Eqs. (26-28):

$$D_{g,t} [(\partial^2 C_{g,t} / \partial r^2) + (1/r)(\partial C_{g,t} / \partial r) + (\partial^2 C_{g,t} / \partial z^2)] - r_g = u_{z,t} (\partial C_{g,t} / \partial z) \quad (26)$$

$$D_{l,t} [(\partial^2 C_{l,t} / \partial r^2) + (1/r)(\partial C_{l,t} / \partial r) + (\partial^2 C_{l,t} / \partial z^2)] - r_l = u_{z,t} (\partial C_{l,t} / \partial z) \quad (27)$$

where:

$u_{z,t}$ is the velocity distribution in the tube-side which defined as:

$$u_{z,t} = 2 u_{av,t} [1 - (r/r_1)^2] \quad (28)$$

where: $u_{av,t}$ is the average velocity inside the tube. The boundary layer conditions for Eqs. (26-27) can be written according to the operating mode as follows Eqs (29-33):

(i) Non-wetted mode

$$z = 0, C_{g,t} = 0 \text{ (solvent free-CO}_2\text{)} \quad (29)$$

$$z = 0, C_{l,t} = C_{l,t}^0 \text{ (inlet condition)} \quad (30)$$

$$r = 0, (\partial C_{g,t} / \partial r) = 0 \quad (31)$$

$$r = 0, (\partial C_{l,t} / \partial r) = 0 \quad (32)$$

$$r = r_1, C_{g,t} = C_{g,m} m_g \quad (33)$$

$$r = r_1, (\partial C_{l,t} / \partial r) = 0 \quad (34)$$

(ii) Partially-wetted mode (Eqs 34-38)

$$z = 0, C_{g,t} = 0 \quad (34)$$

$$z = 0, C_{l,t} = C_{l,t}^0 \quad (35)$$

$$r = 0, (\partial C_{g,t} / \partial r) = 0 \quad (36)$$

$$r = 0, (\partial C_{l,t} / \partial r) = 0 \quad (37)$$

$$r = r_1, D_{g,t} (\partial C_{g,t} / \partial r) = D_{g,m}^* (\partial C_{g,m}^* / \partial r) \quad (38)$$

$$r = r_1, D_{l,t} (\partial C_{l,t} / \partial r) = D_{l,m} (\partial C_{l,m} / \partial r) \quad (36)$$

(iii) Fully-wetted mode

In this operating mode, the boundary conditions for partially-wetted mode are applicable for Eqs. (26-27).

6.4. Model validation

6.4.1. Physical absorption

Usually, the experimental data of CO₂ absorption in water was considered in the validation of the theoretical results for physical CO₂ absorption in membrane contactor (Al-Marzouqi et al., 2008b; Wang et al., 2005; Zhang et al., 2006). The reaction rate term in the mass transfer equation can be neglected. Water has high surface tension value and a mild effect on the hydrophobic membrane surface morphology (Lv et al., 2010). Therefore, membrane contactor will not suffer from wetting during CO₂ absorption process at low operating pressure. As such, model results based on non-wetted mode conditions are more acceptable. Fig. 17 demonstrates the experimental data of CO₂ absorption in PP membrane contactor using water with their theoretical results under the non-wetted and fully-wetted modes of operation. Non-wetted mode exhibits an excellent agreement with experimental results. However, non-

wetted mode conditions are inapplicable at high operating pressure due to generation of a thin layer of water in the membrane. Fig. 17 shows the effect of membrane wetting percentage ($x=(\beta/\delta)*100$) on the model validation for physical (water) CO₂ absorption in PTFE membrane contactor at high operating pressure.

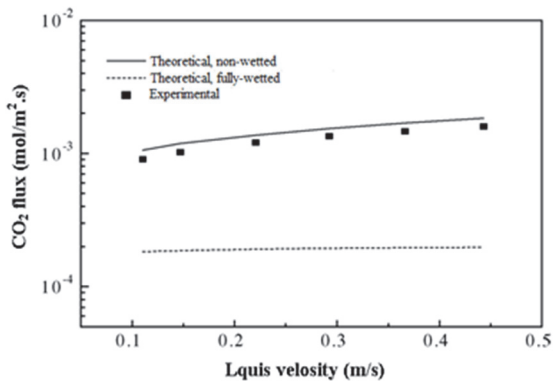


Fig. 16. Experimental and theoretical results of CO₂ absorption in water using polypropylene membrane contactor (Wang et al., 2005)

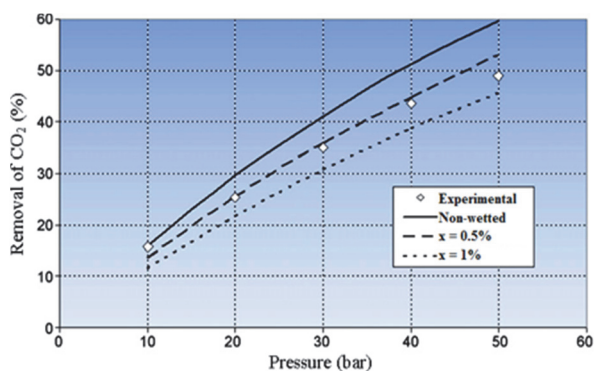


Fig. 17. Model validation for the physical absorption of CO₂ in water at high pressure using PTFE membrane contactor (Faiz and Al-Marzouqi, 2010)

In spite of high wetting resistance of PTFE membrane, model of 0.5% wetting has good agreements with the experimental data than non-wetted mode and 1% wetting. This is because of the presence of ultra-thin layer of water in the membrane pores.

6.4.2. Chemical absorption

Mathematical models were developed for chemical CO₂ absorption using membrane contactors with various solvents (Al-Marzouqi, et al., 2008; Wang et al., 2004b; Wang et al., 2005). Unlike water, conventional CO₂ absorbents (aqueous amine solutions) have high tendency to wet the membrane due to its undesirable chemical and physical properties. Non-wetting mode in membrane contactors is unimplemented for CO₂ chemical absorption even at the same membrane characteristics used in physical absorption. Model includes additional membrane wetting percentage that has more

agreement with the experimental results of long-term CO₂ chemical absorption due to the increasing of solvent penetration through membrane pores (Keshavarz et al., 2008; Zhang et al., 2008). Fig. 18 illustrates the experimental and theoretical results for CO₂ flux change with the operating time in PP membrane contactor using 2M aqueous DEA solution as absorbent. As shown, model results under non-wetted conditions are invalid for all operating time. However, model results with membrane wetting percentage of 6.5%, 9.5% and 10.5% have good agreement with the experimental results for 0, 2 and 4 days, respectively.

At high operating pressure, $x = 0.5\%$ is valid for CO₂ absorption in aqueous solution of 0.1 M MEA, while $x = 1\%$ has good agreement with experimental results for CO₂ absorption in 0.5 M MEA solution (Faiz and Al-Marzouqi, 2010). Both CO₂ absorption experiments were performed in high chemical resistance membrane (PTFE). Therefore, the increasing in x is attributable for the reduction in surface tension value of absorbent when MEA concentration increased.

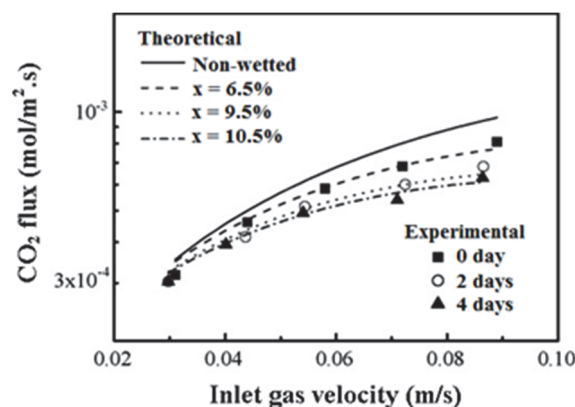


Fig. 18. Experimental and theoretical results for chemical absorption of CO₂ with different operating time (Zhang et al., 2008)

7. Conclusions and recommendation for future research

Membrane gas-liquid contactors for CO₂ absorption application have advantages over conventional technologies due to its high mass transfer which corresponding to the increased of absorption rate. The gas-liquid contacting area can be estimated more easily than other approaches. Furthermore, it allows flexible operating conditions compared to the conventional equipment.

Membrane wetting represents the most influential factor in the commercial application of the membrane technique in a CO₂ absorption system. Factors responsible for membrane wetting should be avoided in order to make this technology more reliable such as low hydrophobicity of membrane surface, larger membrane pore size, higher liquid operating pressure and absorbent of low surface tension. The hydrophobicity of such membrane surfaces can be

improved in two ways: using materials with low surface free energies in membrane fabrication, and/or through the increasing of the membrane surface roughness. PTFE membranes have higher surface hydrophobicity and surface stability compared to the others membranes due to low surface free energy of its material and high chemical stability. However, high fabrication cost and environmental impacts are the main drawbacks of PTFE membranes which make it limited in the industrial large-scale applications.

The wetting resistance of inexpensive membranes can be increased to values comparable to those of PTFE via deposition of rough layer on their surfaces. In spite of the simplicity of this method, it has several disadvantages like expensive and environmentally malignant materials used in this method. The rough layer leads to the increasing of the membrane resistance and membrane pores blockage which reduce the membrane performance. In addition, the adherence of the rough layer may affect by the operating conditions. Therefore, further investigations are required on the influence of operating conditions (gas and liquid flow rates, gas and liquid pressure and temperature) on the performance of deposited layer in long-term CO₂ absorption process. Treatment of membrane surface using plasma to increase its hydrophobicity is superior to other methods. Intensive efforts are required to reduce the cost for plasma treatments method which contributes in commercialization of membrane contactor technology. PVDF membranes with low surface hydrophobicity have lower fabrication cost compared to PTFE. The surface hydrophobicity of PVDF membrane can be improved using low surface energy macromolecule additives in the polymer dope. However, there are few investigations on the surface modification of PVDF membranes in literature and therefore further work is required on producing membranes with high surface hydrophobicity using modified macromolecule additives. The wetting resistance of PVDF membranes can be increased by producing membranes with small pore size and sponge-like structure using a proper non-solvent additive in polymer dope.

Aqueous solutions of amines used as absorbents for CO₂ have potential to membrane wetting due to its low surface tension property. DEA solution has lower impact on the structure of PP membrane pores compared to MEA solution thus DEA maintains better membrane performance than MEA. Mixed amines solutions can improve the absorption efficiency and physical property of absorbent. Amino acid salts solutions meet the membrane contactors requirements in terms of high surface tension value and high CO₂ absorption rate. Amino acid salts increases CO₂ absorption performance of amine solutions as well as enhance the surface tension of solutions when use as promoter additive. Combining of high chemical resistance membrane (PTFE) with activated amine solutions by amino salts could reduce the membrane wetting thus enhance the CO₂ absorption efficiency.

Mathematical model developed under non-wetted mode assumption is implemented for CO₂ absorption in water using hydrophobic membrane contactor. Partially-wetted mode is applicable for CO₂ absorption in aqueous amine solution even using membranes of high surface hydrophobicity and chemical resistance. Model under partially-wetted mode assumption is more practical for CO₂ absorption in water and amine solutions at high operating pressure with different membrane wetting percentage. Mathematical model validation for amino salts solutions is required to investigate its impact on the membrane wetting. In addition, many experimental and theoretical investigations are needed to simulate the real process conditions, including high temperatures, presence of impurities and water vapour in gas feed.

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