HOLLOW FIBER MEMBRANE CONTACTOR ABSORPTION OF CO_2 FROM THE FLUE GAS: REVIEW AND PERSPECTIVE

ZHANG Z.E.[1,2]
YAN Y.F.[1,2,*]
ZHANG L.[1,2]
JU S.X.[1,2]

[1] Key Laboratory of Low-grade Energy Utilization Technologies and Systems
Chongqing University, Ministry of Education of PRC
400044 Chongqing, China
[2] Institute of Energy and Environment, Chongqing University
400044 Chongqing, China

ABSTRACT

With the aggravation of the unprecedented greenhouse effect, the reduction of greenhouse gases which mainly consist of CO_2 has caught high attention by global scholars. The membrane absorption of CO_2 from the flue gas seems a promising alternative to conventional absorption methods like chemical absorption. In this article, the principles of the membrane absorption process were discussed. The research development and current status of CO_2 capture in flue gas using a hollow fiber membrane contactor were reviewed. The affecting factors included the membrane structure and material, module connection form, gas and liquid flow pattern and absorbent. Also, these factors that affected the separation performance of mass transfer processes, as well as the mass transfer coefficients and models for CO_2 absorption were critically discussed in the tube side, shell side and membrane. Also, an experiment system for CO_2 absorption in a membrane contactor was dipicted. The modeling works were validated with experimental results. Additionally, the deficiencies of present development in membrane gas absorption of acid gases and recommendations for future pilot-scale applications were proposed.

Keywords: CO_2 capture, Membrane absorption, Absorbent, Greenhouse effect, Mass transfer.

1. Introduction

Global warming as a threat to the world has been well known for the past decade. With the aggravation of unprecedented greenhouse effect, the reduction of greenhouse gases (GHGs) is highly valued by global researchers. CO_2 in particular, is the most significant anthropogenic greenhouse gas and is responsible for around two-thirds of the greenhouse effects (Nyambura *et al*., 2011; Pan *et al*., 2012; Zhang *et al*., 2008). Fossil fuels, including petroleum, coal and natural gas are all non-renewable resources and contain high percentages of carbon. They are still the major sources of energy throughout the world. A substantial growth of CO_2 emissions over the past 150 years has resulted in a significant increase of the atmospheric CO_2 concentration. The remarkable upward trend in Earth's average temperature could threaten human health, lives and industries associated with the temperature rise (Mavrotas *et al*., 2000; Global CCS Institute, 2011). China as the second-largest economy, for the first time in 2007, emitted more CO_2 than the US leaping to the first of CO_2 emitting countries. Currently owing to the problems of resources, history and technology, Chinese coal consumption accounts for about 75% of the total domestic energy consumption, and coal is expected to be the main raw material

lasts for at least another 50 years (IPCC, 2000). Therefore, it is extremely urgent and important to tackle the air pollution from coal burning.

Generally there are three basic methods to separate CO$_2$ including separation with sorbents or solvents, membranes and cryogenics (Wang *et al.*, 2009). Amongst them, chemical absorption with packed columns is the most well-established method to remove CO$_2$. Normally, the CO$_2$ purity is above 99.9% in the chemical process. And the method of membrane separation saves more energy. So the membrane gas absorption (MGA) technology which combines membrane gas separation with absorption is a new way of contacting liquid and gas for gas separation. This method attracts many researchers' attention due to the operation without limitations caused by foaming, channeling, flooding and entrainment. Membrane gas absorption is a novel method with high efficiency, less required energy and low costs relative to conventional absorption methods (Feron and Jansen, 1997; Hoff, 2003). Furthermore, the hollow fiber membrane contactor (HFMC) has attracted the attention of researchers for the advantages of high-performance absorption, small volume and lightweight (Klaassen, 2005). This paper focuses on the recent progress of the membrane gas absorption of CO$_2$. The factors of the absorption process and mass transfer process are summarized based on the analysis of principle. Furthermore, an experimental program of the high-efficient hollow fiber membrane absorption and desorption of CO$_2$ is proposed with detailed parameters for experiments, simulations and the potentially commercial applications.

2. Principle

The method of membrane absorption is a novel technique under rapid development. The driving force of this technology is the interaction concentration gradient. In the membrane absorption process, the membrane is non-selective of gas and works only as a barrier between the gas stream and the liquid. The selectivity for absorption is provided by the absorbents. The gas mixture and liquid flow on the different side of the fixed gas-liquid interface in a membrane contactor. Gas diffuses from the gas mixture to the gas-liquid interface via the membrane pores without high pressure and then contacts the liquid absorbents on the other side. The CO$_2$-rich solution may be sent into the second membrane contactor for desorption of the absorbed gas. In the meantime, the lean solution is recycled to the absorbent storage which decreases the capital costs (Li and Chen, 2005; Favre and Svendsen, 2012; Fu, 2012).

3. Analysis of transit process

3.1 Material selection

It is very important to consider the effects of membrane materials on the CO$_2$ absorption performance. Selection of the proper polymeric material for membrane gas absorption is of much concern. Generally there are three principal membrane materials including the organic membrane, inorganic membrane and composite membrane. Typical membranes nowadays are prepared from polythene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF), polytetrafluorethylene (PTFE) and poly sulfone (PS) in gas-liquid contacting process. Currently hydrophobic membranes are widely used due to a larger contact area than the hydrophilic membranes. Among these, PTFE together with amine-based solutions are of high hydrophobicity, good mechanical properties and chemical stability.

To study the influences of the parameters involving in the fabrication of a surface modifying macromolecule bended hollow fibers on the membrane performance, Rahbari-Sisakht *et al.* (2012, 2012a, b) successively reported that the surface-modified membrane contactor had better CO$_2$-removal efficiency than the ordinary one. By using a polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) composite membrane with the NaOH aqueous solution for CO$_2$ capture, the results indicated that the inlet liquid pressure and the contact angle increased by 36% and 33% relative to an ordinary membrane, respectively. Meanwhile, the total mass transfer coefficient rose from 5.69×10^{-5} m s^{-1} to 7.56×10^{-5} m s^{-1}

(Wongchitphimon *et al.*, 2011). Never less, the inorganic membrane which provided good thermal and chemical durability could be an alternative of the organic membrane. Meanwhile, the ceramic membrane is considered to be another choice of membrane contactors operating at high temperature. If the membrane surface is modified, the hydrophobic will be improved. A study by Koonaphapdeelert *et al.* (2009) suggested that ceramic hollow fiber membrane contactors were immune from hydrodynamic problems.

3.2 Long-term stability of the membrane

Up till now, the long-term stability of the membrane including the thermal and chemical stability and fouling problems has rarely been reported. In general, organic membranes such as PP and PVDF are tested under about 45 °C. However, this is a significant factor for industrial operations. Moreover, the high membrane thermal stability should be highly valued because the temperature of emitted flue gas is possibly higher than 100 °C. In that case, the membrane may gradually deteriorate at high temperatures. As a result, the membrane thermal stability influences the CO_2 absorption efficiency at different temperatures. The extent of membrane change depends on the glass transition temperature of polymers (T_g). Figure 1 shows the glass-transition temperature of common polymers. It reveals that PI has the highest T_g value, while PE and PP have low values which possibly result in the membrane wettability and instability. Meanwhile, the chemical durability of the membrane has a significant effect on the membrane performance through the long-time operation. Therefore, chemical compatibility between absorbents and membranes should not be ignored. Because there is no convection through the membrane pores and only diffusion of some components happens. Also, the fouling problems are not easy to occur in gas-liquid contactors. In the case of industrial applications, larger gas flow may cause fouling especially as the gas phase flows in the tube. In that case, the pre-filtration is needed to improve the drawbacks. Khaisri *et al.* (2009) examined the MEA solution removal of CO_2 in the gas mixture using three membrane materials, including PP, PTFE and PVDF. Among them, PTFE demonstrated a remarkable stability with time. A long-term stability test for two PVDF membranes was carried out using 2 mol l^{-1} MEA solution over 200 h of operation by Rajabzadeh *et al.* (2013).
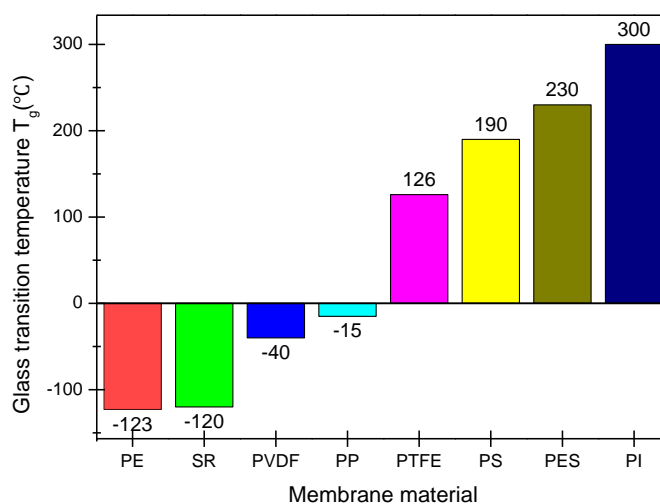
Figure 1. Glass transition temperature of different polymers

3.3 Connection form of membrane modules

The single, serial and parallel membrane modules are intensively studied for research. The series or parallel form performs better than a single one owing to a bigger absorption area. At the same time, a serial way is better than a parallel way because of advancements in absorption stroke and the gas-liquid contact time (Zhang, 2006). In the modeling study on the effects of membrane module arrangement,

Boributh et al. (2011) also found that the sequential form had the best absorption performance among them.

3.4 Membrane structure

In terms of the membrane pore size, hollow fiber membranes consist of porous membranes and non-porous membranes. The porous membrane serves as a boundary between absorbent and gas, however, a non-porous membrane allows one species selectively transferred from one phase to another phase. In general, the CO$_2$ absorption performance of the porous membrane is better than that of the latter one (Al-saffar et al., 1997). Moreover, membranes also can be classified into symmetric membranes, asymmetric membranes and composite membranes in accordance with the characteristics of membrane structures. Normally, symmetric membranes are used since they are easy to cast and offer the intrinsic properties of polymers. But asymmetric and composite membranes are extensively applied in industries which provide good mechanical strength via a thin separation layer (Sridhar et al., 2007). Further, the asymmetric structure of membranes has better removal effect than that of the symmetric structure (Albrecht et al., 2005; Chen et al., 2011).

3.5 Gas and liquid flow pattern

The gas and liquid flow patterns have an important effect on the membrane performance. Generally, there are two flowing modes in a membrane contactor. One mode is that the liquid flows through the tube side (inside of the membrane) while the gas mixture flows in the shell side (outside of the membrane). In contrast, another mode is that the gas flows through the tube, whereas the solution flows through the shell. Zhu et al. (2003) applied a PP hollow fiber membrane to investigate the liquid flow process effect on CO$_2$ separation from the mixture of CO$_2$/N$_2$. The results showed that the removal rate of the tube side was approximately 30% higher than that of the shell side, which indicated the first mode had a better removal effect.

Wang and Cussler (1993) first carried out the membrane separation experiments under different flow modes. In terms of the different flow modes of the gas-liquid phase, they could be divided into cross flow and longitudinal flow. A large amount of researchers investigated in counter-current flow owing to its better mass transfer efficiency. The mass-transfer efficiency of a countercurrent flow improved by 20% than that of the co-current flow under the same test conditions (Rajabzadeh et al., 2009). In a fixed gas-liquid ratio, Zhang et al. (2010) studied the MEA solution to test the influence of the flow modes on the absorption of CO$_2$ performance. When the volume of the absorption solution was large and the inlet and outlet concentrations of the absorbent remained changeless, the absorption process was scarcely affected by the flow mode of gas-liquid phase. As far as the recent research status, the countercurrent flow is usually superior to co-current flow in parallel conditions. When the gas mixture flows inside the tube, membrane pores will be plugged by the massive impurities in the flue gas. Thus, generally the absorbent flows inside the tube and the gaseous mixture flows in the shell (Zhang and Cussler, 2004).

3.6 Absorbent selection

The progress of absorbents is one of major important respects for membrane gas absorption. Generally the liquid absorbents include physical absorbents and chemical absorbents. The selection of absorbent should be considered some criteria including the reactivity, absorption ability and regeneration performance towards CO$_2$ and the physicochemical parameters containing the viscosity, the surface tension and good compatibility with membrane materials (Yan et al., 2014). Surface tension and chemical compatibility with membrane materials are major factors in selecting the solution in the gas-liquid contact process. It can be seen that the surface tension follows the order: physical solutions<chemical solutions<amino acid salts<blended absorbents. The blend has the highest surface tension which is close to water (Lu et al., 2010a). Fu and Zhong (2010) found that the surface tension would follow a downward monotonic trend with increasing the temperature and the alcohol amine concentration.

The aqueous amine-based solutions are usually applied in membrane absorption of CO_2 and MEA is the most commonly used amongst them. Wang *et al.* (2004) numerically analyzed CO_2 removal by the absorption of aqueous DEA, AMP and MDEA solutions in hollow fiber membrane contactors, and found that DEA and AMP solutions had much higher CO_2 absorption fluxes than MDEA. CO_2 from the flue gas was captured and simulated by using a hydrophobic PVDF membrane contactor by Lai *et al.* (2012). When improving the concentration and flow rate of liquid, the CO_2 separation efficiency increased; while when increasing the gas flow rate and CO_2 concentration, it decreased. Meanwhile, it has been obtained that the separation efficiency sequence of alkanolamine solution was NaOH>MEA>DEA>TEA using a hollow fiber membrane for absorbing CO_2 from the gas mixture (Sun *et al.*, 2005). At the same time, in order to reduce the energy consumption and make the absorbent recycled, it has been found that the desorption rate was GLY<MEA<MDEA (Yuan *et al.*, 2004; Zhang *et al.*, 2007). Using the alcohol amine solution absorption and desorption of CO_2, Yang *et al.* (2009) investigated the desorption efficiency of MEA，MDEA and MMEA solution. Additionally Lu *et al.* (2013) recently obtained an order in regeneration efficiency of PG<AMP/PG<AMP in the membrane modules. The regeneration units included a vacuum desorption, a hot regeneration unit and an inlet gas sweep. For a single absorbent, the CO_2 absorption performance order is NaOH>TEPA>TETA>DETA>GLY>MEA>DEA>DIPA>AMP>TEA>MDEA>K_2CO_3, and the CO_2 regeneration performance order is TEA>MDEA>DEA>AMP>DIPA>MEA>NaOH.

In addition, the blended absorbents have been investigated rapidly in order to improve the CO_2-removal performance. Lu *et al.* (2005, 2010, 2010a) studied the absorption performance of blended solutions based on the amino and inorganic-amino acid salts in a hydrophobic microporous membrane. Lin *et al.* (2008) used AMP with the activator PZ and found that with an increase in the additive concentration, the CO_2 absorption rate constantly improved. Zhang *et al.* (2012) investigated the mixed alcohol amine solution absorption of CO_2 in flue gas and reported that the activation effect of MDEA was MDEA/DETA>MDEA/PZ>MDEA/MEA. Meanwhile, the MEA/AMP solution performed well, while the removal effect of MEA/TEA solution was the worst under the same conditions (Paul *et al.*, 2008; Zhang *et al.*, 2010). By performing the absorption and regeneration characteristics of different proportion of miscellaneous absorbents, adding quantity activators into the tertiary amine showed the best performance. Therefore, improvements are necessary for absorbents with high absorption and regeneration rate. Table 1 displays the common membrane absorption test conditions and parameters.

4. Analysis of mass transfer

The CO_2 removal rate is an important measure for absorption performance of the system and absorbents.

$$n_{CO_2} = \frac{V_{in} - V_{out}}{V_{in}} \times 100\% \qquad (1)$$

The overall mass transfer resistance includes the resistance of liquid phase, gas phase and the membrane. Figure 2 describes the mass transfer process in a HFMC. When the system achieves balance, the total mass-transfer coefficient equation is given below:

$$S = \frac{(dw/dt)_{max}(dw/dt)_{mean}}{T_i^2 T_b} \qquad (2)$$

where K_G denotes the total mass transfer coefficient; k_g, k_M and k_l are the individual mass transfer coefficients of gas phase, membrane and liquid phase, respectively; m represents the distribution coefficient between the liquid and gas; and β is the enhancement factor for chemical reaction. In addition, the individual mass transfer coefficient could be determined independently.

Table 1. Conditions used in membrane gas absorption processes

Absorbent	Flue gas component	Material	Reference	Comment
H$_2$O, MEA, DEA, EDA, TEPA, TETA, DETA, NaOH	10%CO$_2$, 90%CH$_4$	PP, SR	Al-Marzouqi, 2009; Al-Marzouqi *et al.*, 2008,2008a	Developed a 2D mathematical model for transport of CO$_2$ via a HFMC
MEA, H$_2$O	12%CO$_2$, 88%N$_2$	PVDF	Boributh *et al.*, 2013	Presented analytical solutions for predicting average wetting ratios
MEA	14-15%CO$_2$, 85-86%N$_2$	PTFE, PP, PVDF, Nylon	Chabanon *et al.*, 2013	Performed experiments on mini-modules and pilot-scale modules (10 m^2 module)
AMP/MEA/PZ	1-9.5%CO$_2$, 90.5-99%N$_2$	PTFE	Chen *et al.*, 2010, 2011	Compared asymmetric membranes and symmetric membranes
MEA	9.5-15.2%CO$_2$, 84.9-90.5%air	PTFE	deMontigny *et al.*, 2006	Connected three modules in series
MEA	10%CO$_2$, 10%H$_2$S, 80%CH$_4$	PVDF, PP	Faiz and Al-Marzouqi, 2009	Considered both partial-wetting and non-wetting conditions
K$_2$CO$_3$	5%CO$_2$, 5%H$_2$S, 90%CH$_4$	PP	Faiz and Al-Marzouqi, 2011	Using two membrane modules in series
MEA, MDEA	0-10%CO$_2$, 90-100%N$_2$	PTFE	Hoff *et al.*, 2004; Hoff and Svendsen, 2013	Compared membrane contactors with absorption towers
MEA	15%CO$_2$, 85%air	PTFE, PP, PVDF	Khaisri *et al.*, 2009	Performed three membranes in membrane absorption systems
MEA	Pure CO$_2$	PTFE	Khaisri *et al.*, 2011, 2011a	Tested absorption and desorption experiments
MDEA/PZ, AMP/PZ	1-15%CO$_2$, 85-99%N$_2$	PVDF, PP	Lin *et al.*, 2008, 2009, 2009a	Investigated composite absorbents in a gas absorption membrane
AMP, PG, AMP/PG	20%CO$_2$, 80%N$_2$	PP	Lu *et al.*, 2013	Set up an experimental system with three generation units
Deionized water, MEA, MDEA	40%CO$_2$, 60%N$_2$	PP	Lv *et al.*, 2009	Observed the effects of factors on removal and mass-transfer rates
MEA	20%CO$_2$, 80%N$_2$	PP	Lv *et al.*, 2012	Coating on the membrane surface to improve its hydrophobicity
NaHCO$_3$, NaOH	10% CO$_2$, 90%CH$_4$	PP, SR	Marzouk and Al-Marzouqi, 2010	Introduced an analyzer monitoring of CO$_2$ in gas streams
H$_2$O, NaOH, MEA, DEA, TETA	9.5%CO$_2$, 90.5% CH$_4$	PTFE	Marzouk *et al.*, 2010a	Evaluation of gas removal at a percentile level
MEA	Pure CO$_2$	PVDF	Rajabzadeh *et al.*, 2009	Studied seven kinds of PVDF HFMCs
Salt water, Fresh water	25%CO$_2$, 75%N$_2$	PI	Sun, 2005	Compared different physical absorbents
NaOH, MEA, DEA, TEA	Pure CO$_2$	PS, SR	Sun *et al.*, 2005, 2007	Investigated the mass transfer process
MEA, PG	CO$_2$ (≤0.5%) in air	PP	Zhang *et al.*, 2010	Observed a low CO$_2$ concentration

Note: PI—polyimide; SR—silicon rubber; GLY-amino acid potassium; MEA-ethanol amine; DEA-diethanol amine; DIPA-diisopropanol amine; AMP-steric hindered amine; TEA-tri-ethanolamine; MDEA-methyldiethanolamine; EDA-ethidene diamine; DETA-diethylenetriamine; TETA-Ethanediamine; TEPA-tetraethylenepen-tamine; MMEA-methylmonoethanolamine; PG-ammonia potassium acetate; PZ-piperazine.
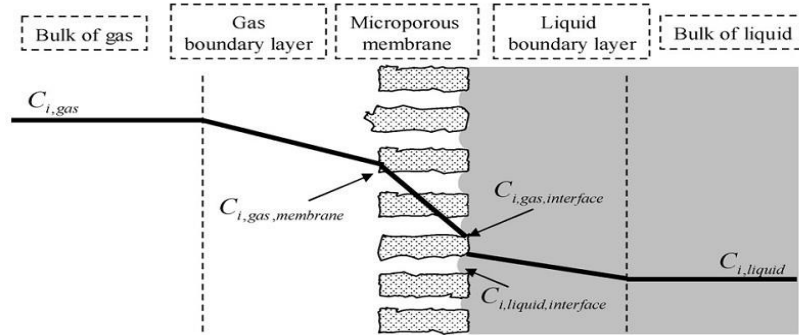
Figure 2. Mass-transfer modeling in membrane contactors for CO_2 absorption (Zhang *et al.*, 2008)

4.1 Mass-transfer coefficients

4.1.1 Liquid side mass transfer coefficient

For a fully developed laminar fluid inside the tube, when only physical absorption occurs, the liquid phase mass transfer coefficient could be estimated by:

$$Sh_l = \frac{k_l^* d_e}{D_l} = 1.62 \left(\frac{d_1^2 v_{absorbent-tube}}{LD} \right)^{0.33}$$ (3)

in which d_e stands for the hydraulic diameter; D_l is the diffusion coefficient of liquid; $v_{absorbent-tube}$ is the velocity of absorbent in the tube; d_l is the fiber diameter; and D is the membrane module diameter. So when the membrane length and the fiber diameter decline, the liquid mass-transfer coefficient goes up at a constant laminar liquid velocity.

Compared with physical absorption, the mass transfer rate of chemical absorption has obviously improved. Because CO_2 reacts with the solvent in the tube side, which results in changes in the CO_2 concentration distribution and then considerably enhances the liquid mass-transfer coefficient. Thus, the liquid phase mass-transfer coefficient of chemical reactions may be depicted:

$$k_l = \beta k_l^*$$ (4)

$$\beta = \frac{J_{chem}}{J_{phy}}$$ (5)

in which J_{chem} and J_{phy} denote the absorption rate of chemical reaction and physical absorption, respectively. And β could be determined by analytical prediction or numerical calculation.

4.1.2 Membrane mass transfer coefficient

When membrane pores are filled with the gas phase, the membrane mass-transfer coefficient is relevant to the gas diffusion coefficient and the microcellular structure. Generally the microcellular structure of the hollow fiber membrane is complicated, so the membrane mass transfer coefficient could be derived as:

$$k_m = D_{CO_2-membrane} = \frac{D_{CO_2-shell} \times \varepsilon}{\delta \times \tau}$$ (6)

where $D_{CO_2-shell}$ and $D_{CO_2-membrane}$ are the effective diffusion coefficient inside the shell and membrane, respectively; ε, δ and τ are the porosity, thickness of the fiber and tortuosity, respectively.

4.1.3 Gas side mass transfer coefficient

For the gas flowing in the shell, the transport process of CO$_2$ in the fiber is mostly molecular diffusion. Therefore, the gas mass transfer coefficient may be calculated by (Prasad and Sirkar, 1988):

$$Sh_g = \frac{k_g d_e}{D_{CO_2\text{-shell}}} = 5.85(1-\phi)\left(\frac{d_e}{L}\right)Re_g^{0.6}Sc_g^{0.33} \tag{7}$$

where $\varnothing$ is the packing density; L is the membrane length; Sh, Re and Sc are the Sherwood number, the Reynolds number and the Schmidt number, respectively. Eq. (7) shows the hydrodynamics influenced by the packing density has a significant impact on the gas mass-transfer coefficient of the gas phase. Thus, influence factors of the absorption efficiency and mass-transfer effect could be known by the above equations and related experiments. Table 2 shows the mass-transfer coefficients of both gas and liquid side.

4.2 Gas flow rate

Some studies have been conducted to investigate the impact of gas velocity on CO$_2$ separation performance (Bottino *et al.*, 2008; Ismail and Yaacob, 2006; Mavroudi *et al.*, 2006). The simulation results showed that the absorption efficiency increased with an increase of the gas velocity from 300 ml min^{-1} to 600 ml min^{-1}, using 0.005 mol l^{-1} MEA for absorbing CO$_2$ from the gas mixture (Faiz *et al.*, 2011a). Hassanlouei *et al.* (2013) recently investigated the absorption rate as a function of gas flow rate under both complete-wetting and non-wetting conditions. It was observed that as the gas flow rate went up, the CO$_2$ capture efficiency significantly dropped. In addition, Hua *et al.* (2013) performed the effects of the inlet gas flow rate on removal of CO$_2$ at different values of operating pressure.

Above all, it is noted that as the gas flow rate increases, the removal efficiency of CO$_2$ declines. On one hand, increasing the gas flow rate decreases the residence time of gas phase in the HFMC. On the other hand, the increase in the gas velocity results in the reduction of the boundary layer and the improvement of the total mass-transfer rate. With the increase of the pressure and driving force, the removal rate and mass-transfer flux of CO$_2$ go up, however, the total mass transfer coefficient slightly declines. In that case, the status of gas phase is close to a saturated condition at the liquid boundary layer. In addition, the liquid flux could not meet the absorption requirements by restrictions of the existing test conditions. Thus, increasing the gas pressure has a negative effect on the total mass-transfer coefficient.

4.3 Liquid flow rate

Many scholars made great efforts to observe the effects of liquid flow rate and partial pressure on the CO$_2$ capture process (Bakeri *et al.*, 2010; Gong *et al.*, 2006; Kim and Yang, 2000). Lv *et al.* (2012) prepared a PP HFMC for CO$_2$ removal in the flue gas, using a 0.5 mol l^{-1} MEA solution as the absorbent with a constant feed gas flow. On a scale of 5-50 ml min^{-1} liquid flow rates, the CO$_2$-removal rate increased from 45% to 95%. Also, the mass transfer efficiency advanced with an increase in the liquid velocity. Meanwhile, some experimental and modeling results showed that increasing the liquid flow rate promoted the absorption process (Hua *et al.*, 2013). Dindore *et al.* (2005; 2005a) prepared a new type of cross-flow membrane contactor, which was used for chemical absorption of CO$_2$ ranging from 0.25 mol l^{-1} to 0.5 mol l^{-1} K$_2$CO$_3$ solution. They found that as the fluid velocity grew from 0 to 0.12 m s^{-1}, the outlet CO$_2$ concentration gradually declined.

It can be concluded that a higher liquid velocity leads to a lower CO$_2$ concentration in the liquid phase, which in turn results in a higher CO$_2$ concentration gradient between gas and liquid. Because when the gas velocity and pipe diameters are constant, increasing the liquid velocity betters the fluid flow in the membrane which reduces the liquid phase boundary layer. Similarly, the absorption ability of CO$_2$ in the membrane module improves, resulting in the decline of the outlet CO$_2$ concentration and growth in the CO$_2$-removal rate.

Table 2. Reported mass transfer correlations of the liquid and gas

	Equation	Condition	Reference
Liquid mass-transfer coefficient	$Sh_l = 1.64\left(\dfrac{d_e}{L}Re_l\,Sc_l\right)^{0.33}$	Observed the mass transfer in the fiber lumen for gas absorption	Yang and Cussler, 1986
	$Sh_l = 1.62\left(\dfrac{d_e}{L}Re_l\,Sc_l\right)^{0.33}$	Gz>4	Prasad and Sirkar, 1988
	$Sh_l = 1.5\left(\dfrac{d_e}{L}Re_l\,Sc_l\right)^{0.33}$	Obtained from the electrolytes and protein extraction experiments	Dahuron and Cussler, 1988
	$Sh_l = \sqrt[3]{3.67^3 + 1.62^3\left(\dfrac{d_e}{L}Re_l\,Sc_l\right)}$	Carried a microporous hollow fiber module with liquid flow in the fibers; ϕ =0.03, 0.7	Kreulen *et al.*, 1993
	$Sh_l = 0.57\,Re_l^{0.31}\,Sc_l^{0.33}$	Developed a cylindrical fiber module with outside flow of water; 0.01<Re<1	Bhaumik *et al.*, 1998
	$Sh_l = 0.2\left(\dfrac{d_e}{L}\right)^{0.33}Re_l^{1.01}\,Sc_l^{0.33}$	Analysis of Wilson-plot methodology for membrane extraction; Re<34, Gz<65	Viegas *et al.*, 1998
	$Sh_l = \left(0.3045\phi^2 - 0.3421\phi + 0.0015\right)Re_l^{0.9}\,Sc_l^{0.33}$	Observed the influence of packing densities on the mass transfer coefficient; 60<Re<1200; 0.0804≤ ϕ ≤0.702	Wu and Chen, 2000
	$Sh_l = \dfrac{1}{(0.86-0.3\phi)\phi}\,Gz^{(0.3\phi+0.14)}$	Developed a novel random cell module for the shell side mass-transfer performance; the effect of random arrangement is taken into consideration; 60<Re<1200; 0.2≤ ϕ ≤0.5	Zheng *et al.*, 2004
	$Sh_l = 8.38\,Re_l^{-1.81}\,Sc_l^{0.66}$	Conducted the mass transfer and fluids hydrodynamics studies of CO_2 absorption in a membrane contactor; 0.188≤ ϕ ≤0.281	Kartohardjono *et al.*, 2006
	$Sh_l = 1.613\left(\dfrac{d_e}{L}Re_l\right)^{0.92}Sc_l^{0.33}$	Liquid flowing outside the hollow fibers; 60<Re<200; 0.1≤ ϕ ≤0.304	Ozturk and Hughes, 2012

|		
Gas mass-transfer coefficient	$Sh_g = 1.25\left(\dfrac{d_e}{L}Re_g\,Sc_g\right)^{0.33}$	Results for gas absorption; $\phi \leq 0.26$	Yang and Cussler, 1986
	$Sh_g = 5.85(1-\phi)\left(\dfrac{d_e}{L}\right)Re_g^{0.6}\,Sc_g^{0.33}$ (hydrophobic) $Sh_g = 6.1(1-\phi)\left(\dfrac{d_e}{L}\right)Re_g^{0.6}\,Sc_g^{0.33}$ (hydrophilic)	Developed microporous hollow-fiber modules for solvent extraction; $0<Re<500$; $0.04\leq \phi \leq 0.4$	Prasad and Sirkar, 1988
	$Sh_g = \left[0.53-0.58(1-\varepsilon)\right]Re_g^{0.53}\,Sc_g^{0.33}$	Performed a fluid flow and mass-transfer experiments on axial flow hollow fiber modules for gas stripping; $21<Re<324$; $0.32\leq \phi \leq 0.76$	Costello et al., 1993
	$Sh_g = 8.71\left(\dfrac{d_e}{L}\right)Re_g^{0.33}\,Sc_g^{0.74}$	$\phi =0.3$; $0.16\leq Re\leq 7.3$	Viegas et al., 1998
	$Sh_g = 0.09\varepsilon\,Re_g^{(0.64-0.16\varepsilon)}\,Sc_g^{0.33}$	$Re<10$; $0.35\leq \phi \leq 0.79$	Gawronski and Wrzesinska, 2000
	$Sh_g = 2.15\,Re_g^{0.42}\,Sc_g^{0.33}$	Examined the mass transfer inside the shell of a transverse flow hollow fiber module; $0.8\leq Re\leq 20$; $\phi =0.43$	Zheng et al., 2005
	$Sh_g = \left(-0.4575\phi^2 +0.3993\phi -0.0475\right)Re_g^{\left(4.0108\phi^2 -4.4296\phi+1.5585\right)}\,Sc_g^{0.33}$	Observed the laminar liquid flow in an osmotic distillation process; $10<Re<143$; $0.306\leq \phi \leq 0.612$	Thanedgunbaworn et al., 2007

4.4 Feed Concentration and Composition

In general, the CO_2 content in flue gas is a key factor for process selection. Changes in the feed gas concentration directly affect the capture performance. According to the duel-membrane theory, the gas phase boundary layer is thinner with a higher percentage of CO_2. Meanwhile, the overall mass transfer coefficient decreases due to a hindrance to a lot of CO_2 in the membrane pores with increasing the gas phase boundary layer resistance. However, as the CO_2 inlet concentration raises, the CO_2 concentration gradient between the gas phase and the gas-liquid interface also increases. Namely that the diffusion rate and mass transfer rate of CO_2 rise with an increase of the gas phase mass-transfer driving force. Yang *et al*. (2005) examined the real flue gas, and found the mass transfer rate increased with the rise in CO_2 concentration. Because the more CO_2 molecules diffused via membrane pores when the concentration was increased. Similar results can be seen under different CO_2 concentrations (Boributh *et al*., 2011, 2012; Lu *et al*., 2007).

4.5 Absorbent temperature

Commonly, a growth in absorbent temperature may cause some drawbacks on the absorption performance of gas-liquid HFMCs (Golkhar *et al*., 2013). Eslami *et al*. (2011) simulated ammonia potassium acetate and PTFE hollow fiber membrane absorption CO_2 from the power plant flue gas. Under the conditions of 0.5 mol l^{-1} liquid concentration and the liquid temperature changing from 303 K to 323 K, it turned out that increasing the liquid temperature hindered the dissolution of gases, but promoted the liquid evaporation. Thus the total mass transfer efficiency and the removal rate decreased. Shirazian *et al*. (2009) compared the removal rate with a constant fluid velocity at the temperatures of 298 K and 288 K. The CO_2-removal rate increased about 10% with the lower temperature. Thus the CO_2 removal rate significantly dropped and the diffusion rate went up by increasing the liquid temperature due to the reduction of CO_2 solubility in absorbents.

4.6 Fiber membrane length

With the constant numbers and diameters of the HFMC, the growth of the membrane length results in increasing the surface area and the residence time in the liquid phase, which is conducive to the chemical reaction. If the length is much too long, the liquid tends to saturation leading to reducing the liquid mass-transfer driving force and the mass transfer efficiency. Boributh *et al*. (2011a) investigated three membrane lengths of 0.25, 0.5 and 0.7m, and reported that using the length of 0.7m, the CO_2 removal rate increased by 15.27% and 3.58% in comparison with other two modules, respectively. Also, Kumar *et al*. (2002) observed the impact of the fiber length on the absorption flux to validate the numerical models with experiments.
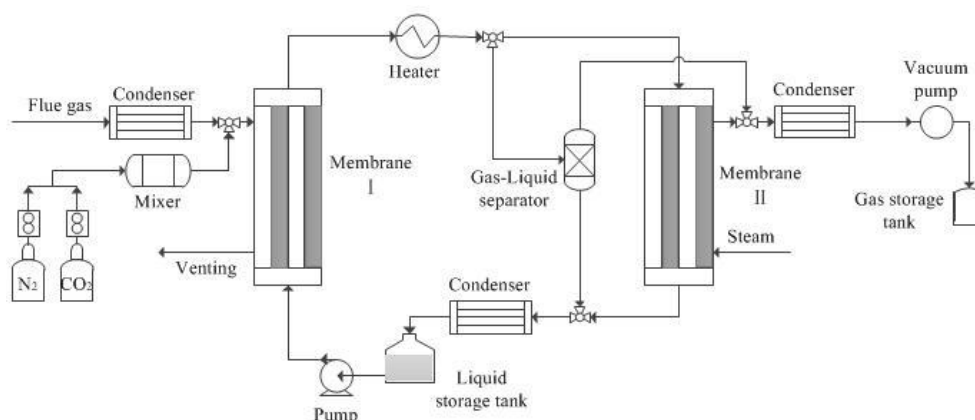
Figure 3. A schematic diagram of hollow fiber membrane absorption of CO_2

In order to investigate on the absorption and desorption characteristics of membrane gas absorption and traditional separation methods, an experiment system of CO_2 separation in a HFMC is proposed and depicted in Figure 3. Meanwhile, it is the first time to handle with the actual flue gas emissions of coal, the natural gas or biogas in a single membrane, serial membranes or parallel membranes in one system. An investigation on influences of the vacuum degree and a comparison between the traditional and novel regenerative method is achieved. The recovery characteristics of CO_2 in the distinct blowing atmosphere are also realized. This experimental process consists of the flue gas condensation, gas membrane absorption and CO_2 desorption stage. Firstly, the coal-fired flue gas after cooling is sent into the membrane contactor, and then reacts with a counter current absorbent. The rich solution is heated by a heater, and flows into the other membrane contactor or a gas-liquid separator. Absorbed CO_2 will be released out of the solvent. Whereas the lean solution returns back to the liquid storage tank, and continues to flow into the whole system. Thus, high concentration of CO_2 could be collected through the vacuum pump by controlling vacuum degree. Moreover, it is easy to take samplings from the input and output of the membrane contactor. Using the deionized water and 0.5 mol l^{-1} MEA as absorbents, Figure 4 indicates that the CO_2-removal rate goes up with increasing the MEA solution velocity varied from 0.05 to 0.5 m s^{-1}. And serial membrane contactors have the best absorption capacity of CO_2.
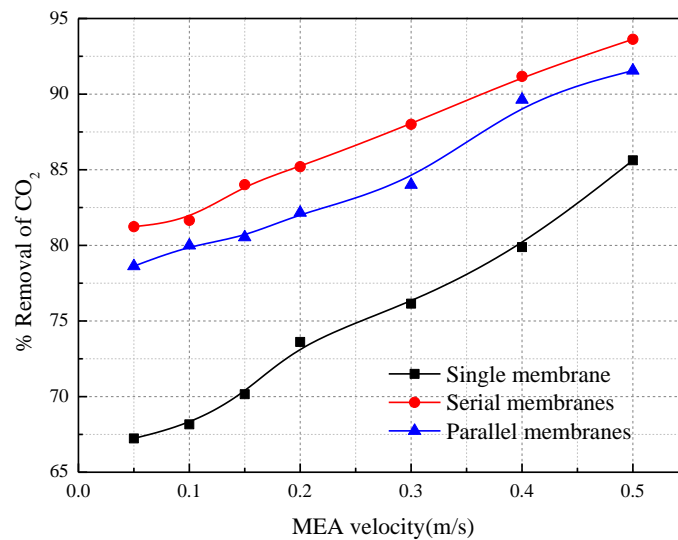
Figure 4. Influence of MEA velocity on the CO_2 removal efficiency
(feed compositions: CO_2:N_2 = 14%:86%; gas pressure: 105 kPa; v_g: 0.1 m s^{-1})

5. Physical and mathematical models for membrane absorption

A two-dimensional mathematical model for membrane absorption CO_2 has been developed in recent literatures (Al-Marzouqi *et al*., 2008, 2008a; Rajabzadeh *et al*., 2009, 2013; Ghadiri *et al*., 2013). In most cases, it is assumed that the absorbent flows inside the tube, while the gas mixture is fed to in the shell side in a countercurrent mode, as shown in Figure 5. Thus, CO_2 is removed from the gas mixture by diffusion through the membrane pores and reacting with the solution inside the tube.

In order to predict the transport of CO_2 in a HFMC, this model is built on the basis of the following assumptions:

 (1) The system is under steady-state and isothermal conditions.

 (2) A fully developed laminar parabolic gas velocity profile is adopted, whereas a laminar liquid flows in the lumen of hollow fibers on the contrary.

(3) The Henry's law is applicable for the gas-liquid surface.

(4) The gas is regarded as an ideal gas.

(5) The Newtonian-type fluid inside the lumen has constant physical properties
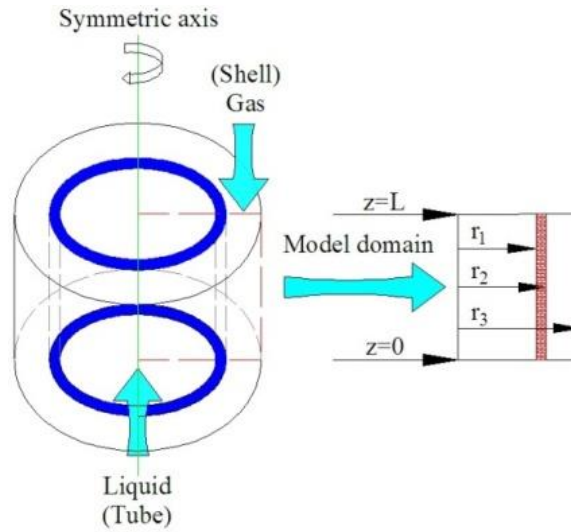
Figure 5. A schematic representation of the membrane contactor used for modeling

5.1 Tube side equations

Based on the above assumptions, the steady state continuity equation for the transport and reaction of those two species in the tube side due to diffusion, reaction and convection so it can be derived as：

$$D_{i\text{-tube}}\left[\frac{\partial^2 C_{i\text{-tube}}}{\partial r^2}+\frac{1}{r}\frac{\partial C_{i\text{-tube}}}{\partial r}+\frac{\partial^2 C_{i\text{-tube}}}{\partial z^2}\right]=v_{z\text{-tube}}\frac{\partial C_{i\text{-tube}}}{\partial r}-R_i \tag{8}$$

in which i denotes CO_2 or absorbent. Meanwhile, where $D_{i\text{-tube}}$, $C_{i\text{-tube}}$, R_i and $v_{z\text{-tube}}$ denote the diffusion coefficient, the concentration, the reaction rate of specie i and the axial velocity inside the fiber, respectively.

The axial velocity distribution inside the tube is assumed to follow the Newtonian laminar flow (Versteeg *et al.*, 1996):

$$v_{z\text{-tube}}=2\bar{v}_{tube}\left[1-\left(\frac{r}{r_1}\right)^2\right] \tag{9}$$

where $\bar{v}_{tube}$ and r_1 are the average gas velocity in the tube side and the inner tube radius, respectively.

5.2 Membrane equations

CO_2 can be diffused in the membrane, because the membrane in this part is considered in a non-wetting mode. So in the case of non-wetting condition, the steady state continuity equation for transport CO_2 inside the membrane could be written as:

$$D_{CO_2\text{-membrane}}\left[\frac{\partial^2 C_{CO_2\text{-membrane}}}{\partial r^2}+\frac{1}{r}\frac{\partial^2 C_{CO_2\text{-membrane}}}{\partial r}+\frac{\partial^2 C_{CO_2\text{-membrane}}}{\partial z^2}\right]=0 \tag{10}$$

Here , $D_{CO_2\text{-membrane}}$ is the diffusion coefficient in the membrane.

5.3 Shell side equations

The continuity equation for steady state for the transport CO_2 inside the shell side where only CO_2 flows could be defined as:

$$D_{CO_2\text{-membrane}}\left[\frac{\partial^2 C_{CO_2\text{-membrane}}}{\partial r^2} + \frac{1}{r}\frac{\partial^2 C_{CO_2\text{-membrane}}}{\partial r} + \frac{\partial^2 C_{CO_2\text{-membrane}}}{\partial z^2}\right] = 0 \tag{11}$$

According to the Happel's free surface theory, the axial velocity $v_{z\text{-shell}}$ in the shell may be estimated (Happel, 1959):

$$v_{z\text{-shell}} = 2\bar{v}_{shell}\left[1 - \left(\frac{r_2}{r_3}\right)^2\right]\left[\frac{(r/r_3)^2 - (r_2/r_3)^2 + 2\ln(r_2/r)}{(r_2/r_3)^4 - 4(r_2/r_3)^2 + 4\ln(r_2/r_3) + 3}\right] \tag{12}$$

in which $\bar{v}_{shell}$ and r_2 are the gas average velocity inside the shell side and outer fiber radius, respectively. At the same time, the inner shell radius r_3 may be written as:

$$r_3 = r_2\sqrt{\frac{1}{1-\phi}} \tag{13}$$

$$1-\phi = \frac{nr_2^2}{R^2} \tag{14}$$

here n and R denote the number of fibers and the inner module radius, respectively.

Extensive authors have simulated absorption of CO_2 from the mixed gases using this finite element method. Systems of CO_2-H_2O, CO_2-MEA, CO_2-DEA, CO_2-AMP, CO_2-MDEA, CO_2-K_2CO_3, CO_2-NaOH have been reported. Then the CO_2-MEA system in a non-wetting mode is modeled. Figures 6 (a) and (b) show the concentration distribution of CO_2 and the MEA solution. The mixed gas flows from the shell side of the membrane at the highest CO_2 concentration, while MEA is fed to the tube inlet where the CO_2 concentration is assumed zero and the liquid concentration is highest. In addition, other acid gases such as H_2S, SO_2 have been studied using the same method (Fasihi *et al.*, 2012; Rezakazemi *et al.*, 2011; Faiz and Al-Marzouqi, 2009, 2011). So this model shows a great potential in separation of sour gases.

(a)   (b)
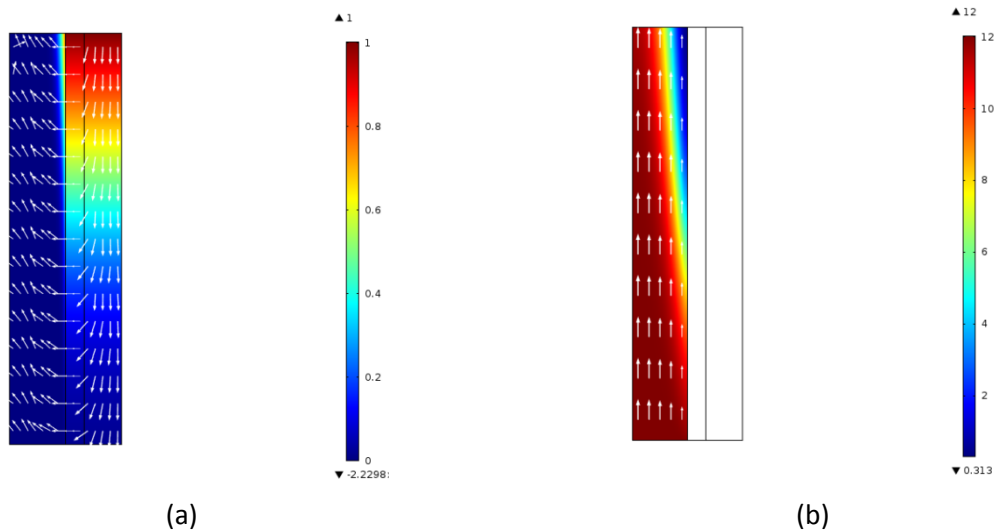
Figure 6. Model solution for (a) CO_2 and (b) MEA (C_g: 4 mol m⁻³, C_{MEA}: 12 mol m⁻³, v_{MEA}: 0.5 m s⁻¹)

6. Conclusions

Undoubtedly, hollow fiber membrane gas absorption technology has been extensively applied in industrial sectors as well as laboratories, for instance, removal of acidic gases and VOCs recovery. Currently, membrane absorption applications in gas separation for wide-spread industrialization are difficult to implement because of the existing technical and economic issues. For scale-up applications, three major limitations of membrane gas absorption are focused on the following aspects:

The design of membrane structure and selection of membrane materials are the key to success of the industrialization of membrane gas absorption technology. New membrane materials with the resistance to high-temperatures, the corrosion and pollutions are desired to develop. The improvement of novel membrane materials could play a vital role in future of HMFCs. It is necessary to develop a cost-effective material, with good mechanical strength, high hydrophobicity and long-term stability. In addition, it should consider not only the performance of the material, but also the compatibility with the material. Basically ideal absorbents should have a good removal ability and regeneration performance, and are of low toxicity, inexpensive and easy to recycle. There is a limitation of the trade-off between cost and separation performance in the application of membrane contactors for gas absorption.

The composition of the real flue gas is a key factor for membrane gas absorption of CO_2. There is a need to reach a system with real operational conditions. High oxygen content in the feed gas can result in excessive amine loss. Coal-fired power plant flue gas may contain SO_2, H_2S, H_2O and CH_4. In particular, O_2 and SO_2 also show significant influences on the liquid solutions. Meanwhile, fly ash and high temperatures have negative impacts on absorption efficiency. Thus, it is important to pretreat the gas mixture for the viability of commercialized applications in further researches. Generally, in most of previous researches, the operation temperature is ambient temperature. However, in practice, these works are conducted at much higher temperatures. It should be noted that increasing the operation temperature reduces the CO_2 solubility and membrane stability, and causes the degradation of absorbents. Therefore, the possibility is worthy of attention to operate at high temperatures, even over 100 °C

In the meantime, optimizing the mathematical models and facilitating the commercialization of this post-combustion carbon capture technology are necessary. Optimizing the absorption processes and the mass transfer models owing to difference in the materials and structures of the membrane modules and a comprehensive economic analysis of the membrane gas absorption are constantly required. However, these are seldom taken into account in previous works. The investigation on the mass-transfer coefficients of the membrane contactor is also important which may offer theoretical basis for modeling and experimental works.

References
Albrecht W., Hilke R., Kneifel K., Weigel T. and Peinemann K. (2005), Selection of microporous hydrophobic membranes for use in gas/liquid contactors: An experimental approach, *Journal of Membrane Science,* **263**, 66-76.

Al-Marzouqi M., El-Naas M., Marzouk S. and Abdullatif N. (2008), Modeling of chemical absorption of CO_2 in membrane contactors, *Separation and Purification Technology*, **62**, 499-506.

Al-Marzouqi M.H., El-Naas M.H., Marzouk S.A.M. and Abdullatif N. (2008a), Modeling of CO_2 absorption in membrane contactors, *Separation and Purification Technology*, **59**, 286-293.

Al-Marzouqi M.H., Marzouk S.A.M., El-Naas M.H. and Abdullatif N. (2009), CO_2 removal from CO_2-CH_4 gas mixture using different solvents and hollow fiber membranes, *Industrial & Engineering Chemistry Research*, **48**, 3600-3605.

Al-saffar H.B., Ozturk B. and Hughes R. (1997), A comparison of porous and non-porous gas-liquid membrane contactors for gas separation, *Institution of Chemical Engineers*, **75**, 685-692.

Bakeri G., Ismail A.F., Shariaty-Niassar M. and Matsuura T. (2010), Effect of polymer concentration on the structure and performance of polyetherimide hollow fiber membranes, *Journal of Membrane Science*, **363**, 103-111.

Bhaumik D., Majumdar S.and Sirkar K.K. (1998), Absorption of CO$_2$ in a transverse flow hollow fiber membrane module having a few wraps of the fiber mat, *Journal of Membrane Science*, **138**, 77-82.

Boributh S., Assabumrungrat S., Laosiripojana N. and Jiraratananon R. (2011), Effect of membrane module arrangement of gas–liquid membrane contacting process on CO$_2$ absorption performance: A modeling study, *Journal of Membrane Science,* **372**, 75-86.

Boributh S., Assabumrungrat S., Laosiripojana N. and Jiraratananon R. (2011a), A modeling study on the effects of membrane characteristics and operating parameters on physical absorption of CO$_2$ by hollow fiber membrane contactor, *Journal of Membrane Science,* **380**, 21-33.

Boributh S., Jiraratananon R. and Li K. (2013), Analytical solutions for membrane wetting calculations based on log-normal and normal distribution functions for CO$_2$ absorption by a hollow fiber membrane contactor, *Journal of Membrane Science,* **429**, 459-472.

Boributh S., Rongwong W., Assabumrungrat S., Laosiripojana N. and Jiraratananon R. (2012), Mathematical modeling and cascade design of hollow fiber membrane contactor for CO$_2$ absorption by monoethanolamine, *Journal of Membrane Science,* **401-402**, 175-189.

Bottino A., Capannelli G., Comite A., Di Felice R. and Firpo R. (2008), CO$_2$ removal from a gas stream by membrane contactor, *Separation and Purification Technology*, **59**, 85-90.

Chabanon E., Kimball E., Favre E., Lorain O., Goetheer E., Ferre D., Gomez A. and Broutin P. (2013), Hollow fiber membrane contactors for post-combustion CO$_2$ capture: A scale-up study from laboratory to pilot plant, *Oil & Gas Science and Technology*, doi: 10.2516/ogst/2012046.

Chen S.C., Lin S.H., Chien R.D. and Hsu P.S. (2010), Effects of shape, porosity, and operating parameters on carbon dioxide recovery in polytetrafluoroethylene membranes, *Journal of Hazardous Materials*, **179**, 692-700.

Chen S.C., Lin S.H., Chien R.D., Wang Y.H. and Hsiao H.C. (2011), Chemical absorption of carbon dioxide with asymmetrically heated polytetrafluoroethylene membranes, *Journal of Environmental Management*, **92**, 1083-1090.

Costello M.J., Fane A.G., Hogan P.A. and Schofield R.W. (1993), The effect of shell side hydrodynamics on the performance of axial flow hollow fibre modules, *Journal of Membrane Science,* **80**, 1-11.

Dahuron L. and Cussler E.L. (1988), Protein extractions with hollow fibers, *AIChE Journal*, **34**, 130-136.

DeMontigny D., Aboudheir A., Tontiwachwuthikul P. and Chakma A. (2006), Using a packed-column model to simulate the performance of a membrane absorber, *Industrial & Engineering Chemistry Research*, **45**, 2580-2585.

Dindore V.Y. and Versteeg G.F. (2005a), Gas-liquid mass transfer in a cross-flow hollow fiber module: Analytical model and experimental validation, *International Journal of Heat and Mass Transfer*, **48**, 3352-3362.

Dindore V.Y., Brilman D. and Versteeg G. (2005), Modeling of cross-flow membrane contactors: Mass transfer with chemical reactions, *Journal of Membrane Science*, **255**, 275-289.

Eslami S., Mousavi S.M., Danesh S. and Banazadeh H. (2011), Modeling and simulation of CO$_2$ removal from power plant flue gas by PG solution in a hollow fiber membrane contactor, *Advances in Engineering Software*, **42**, 612-620.

Faiz R. and Al-Marzouqi M. (2009), Mathematical modeling for the simultaneous absorption of CO$_2$ and H$_2$S using MEA in hollow fiber membrane contactors, *Journal of Membrane Science,* **342**, 269-278.

Faiz R. and Al-Marzouqi M. (2011), Insights on natural gas purification: Simultaneous absorption of CO$_2$ and H$_2$S using membrane contactors, *Separation and Purification Technology*, **76**, 351-361.

Faiz R., El-Naas M.H., Al-Marzouqi M. (2011a), Significance of gas velocity change during the transport of CO$_2$ through hollow fiber membrane contactors, *Chemical Engineering Journal*, **168**, 593-603.

Fasihi M., Shirazian S., Marjani A. and Rezakazemi M. (2012), Computational fluid dynamics simulation of transport phenomena in ceramic membranes for SO$_2$ Separation, *Mathematical and Computer Modeling*, **56**, 278-286.

Favre E. and Svendsen H.F. (2012), Membrane contactors for intensified post-combustion carbon dioxide capture by gas–liquid absorption processes, *Journal of Membrane Science*, **407-408**, 1-7.

Feron P.H.M. and Jansen A.E. (1997), The production of carbon dioxide from flue gas by membrane gas absorption, *Energy Conversion and Management*, **38**, 93-98.

Fu D. and Zhong Z.K. (2010), Experimental study on the surface tension of diethanolamine-n-methyldiethanolamine-water mixtures, *Acta Chimica Sinica*, **68**, 1241-1246.

Gawronski R. and Wrzesinska B. (2000), Kinetics of solvent extraction in hollow-fiber contactors, *Journal of Membrane Science*, **168**, 213-222.

Ghadiri M., Marjani A. and Shirazian S. (2013), Mathematical modeling and simulation of CO_2 stripping from monoethanolamine solution using nano porous membrane contactors, *International Journal of Greenhouse Gas Control*, **13**, 1-8.

Global CCS Institute. (2011), The Global Status of CCS: 2011, Canberra, Australia.

Golkhar A., Keshavarz P. and Mowla D. (2013), Investigation of CO_2 removal by silica and CNT nanofluids in microporous hollow fiber membrane contactors, *Journal of Membrane Science*, **433**, 17-24.

Gong Y., Wang Z. and Wang S. (2006), Experiments and simulation of CO_2 removal by mixed amines in a hollow fiber membrane module, *Chemical Engineering and Processing: Process Intensification*, **45**, 652-660.

Happel J. (1959), Viscous flow relative to arrays of cylinders, *AIChE Journal*, **5**, 174-177.

Hassanlouei R.N., Pelalak R. and Daraei A. (2013), Wettability study in CO_2 capture from flue gas using nano porous membrane contactors, *International Journal of Greenhouse Gas Control,* **16**, 233-240.

Hoff K.A. (2003), Modeling and experimental study of carbon dioxide absorption in a membrane contactor. Ph.D. Thesis, Department of Chemical Engineering, Norwegian University of Science and Technology.

Hoff K.A. and Svendsen H.F. (2013), CO_2 absorption with membrane contactors vs. packed absorbers-challenges and opportunities in post combustion capture and natural gas sweetening, *Energy Procedia*, **37**, 952-960.

Hoff K.A., Juliussen O., Falk-Pedersen O. And Svendsen H.F. (2004), Modeling and experimental study of carbon dioxide absorption in aqueous alkanolamine solutions using a membrane contactor, *Industrial & Engineering Chemistry Research*, **43**, 4908-4921.

Hua C.G., Kang G.D., Jia J.X., Li M., Cao Y.M. and Yuan Q. (2013), Physical absorption of CO_2 using polyvinylidene fluoride membrane contactor at high pressure and mathematical simulation, *Chemical Journal of Chinese Universities*, **34**, 906-912.

IPCC. (2000), Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories, IPCC-TSU NGGIP, Japan.

Ismail A.F. and Yaacob N. (2006), Performance of treated and untreated asymmetric polysulfone hollow fiber membrane in series and cascade module configurations for CO_2/CH_4 gas separation system, *Journal of Membrane Science*, **275**, 151-165.

Kartohardjono S., Nata P.A., Prasetio E. and Yuliusman (2006), Performance of hollow fiber membrane gas-liquid contactors to absorb CO_2 using diethanolamine (DEA) as a solvent, *Makara Seri Teknologi*, **13**, 86-90.

Khaisri S., deMontigny D., Tontiwachwuthikul P. and Jiraratananon R. (2009), Comparing membrane resistance and absorption performance of three different membranes in a gas absorption membrane contactor, *Separation and Purification Technology*, **65**, 290-297.

Khaisri S., deMontigny D., Tontiwachwuthikul P. and Jiraratananon R. (2011), Membrane contacting process for CO_2 desorption, *Energy Procedia*, **4**, 688-692.

Khaisri S., deMontigny D., Tontiwachwuthikul P. and Jiraratananon R. (2011a), CO_2 stripping from monoethanolamine using a membrane contactor, *Journal of Membrane Science*, **376**, 110-118.

Kim Y.S. and Yang S.M. (2000), Absorption of carbon dioxide through hollow fiber membranes using various aqueous absorbents, *Separation and Purification Technology*, **21**, 101-109.

Klaassen R., Feron P.H.M. and Jansen A.E. (2005), Membrane contactors in industrial applications, *Chemical Engineering Research and Design*, **83**, 234-246.

Koonaphapdeelert S., Wu Z.T. and Li K. (2009), Carbon dioxide stripping in ceramic hollow fibre membrane contactors, *Chemical Engineering Science*, **64**, 1-8.

Kreulen H., Smolders C.A., Versteeg G.F. and van Swaaij W.P.M. (1993), Microporous hollow fibre membrane modules as gas-liquid contactors. part 1. physical mass transfer processes: A specific application: mass transfer in highly viscous liquids, *Journal of Membrane Science*, **78**, 197-216.

Kumar P.S., Hogendoorn J.A., Feron P.H.M. and Versteeg G.F. (2002), New absorption liquids for the removal of CO_2 from dilute gas streams using membrane contactors, *Chemical Engineering Science*, **57**, 1639-1651.

Lai C.F., Yang B., Zhang G.L., Wen C.S., Cao R. and Wu R.R. (2012), Factors influencing CO_2 capture by PVDF membrane contactor, *CIESC Journal*, **63**, 500-507.

Li J. and Chen B. (2005), Review of CO_2 absorption using chemical solvents in hollow fiber membrane contactors, *Separation and Purification Technology*, **41**, 109-122.

Lin S.H., Chiang P.C., Hsieh C.F., Li M.H. and Tung K.L. (2008), Absorption of carbon dioxide by the absorbent composed of piperazine and 2-amino-2-methyl-1-propanol in PVDF membrane contactor, *Journal of the Chinese Institute of Chemical Engineers*, **39**, 13-21.

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

Lin S.H., Tung K.L., Chen W.J. and Chang H.W. (2009a), Absorption of carbon dioxide by mixed piperazine-alkanolamine absorbent in a plasma-modified polypropylene hollow fiber contactor, *Journal of Membrane Science*, **333**, 30-37.

Lu J.G., Hua A.C., Xu Z.W., Li J.T., Liu S.Y., Wang Z.L., Zhao Y.L. and Pan C. (2013), CO_2 capture by membrane absorption coupling process: Experiments and coupling process evaluation, *Journal of Membrane Science,* **431**, 9-18.

Lu J.G., Ji Y., Zhang H. and Chen M.D. (2010), CO_2 capture using activated amino acid salt solutions in a membrane module, *Separation Science and Technology*, **45**, 1240-1251.

Lu J.G., Wang L.J., Sun X.Y., Li J.S. and Liu X.D. (2005), Absorption of CO_2 into aqueous solutions of methyldiethanolamine and activated methyldiethanolamine from a gas mixture in a hollow fiber contactor, *Industrial & Engineering Chemistry Research*, **44**, 9230-9238.

Lu J.G., Zhang H., Ji Y., Fan F. and Liu C. (2010a), Amino acid-salt-based complex absorbents for CO_2 capture in a membrane contactor, *Energy Fuels*, **24**, 4617-4626.

Lu J.G., Zheng Y.F., Cheng M.D. and Wang L.J. (2007), Effects of activators on mass-transfer enhancement in a hollow fiber contactor using activated alkanolamine solutions, *Journal of Membrane Science*, **289**, 138-149.

Lv Y.X., Yu X.H. and Tu S.D. (2009), Experiment of CO_2 separation from flue gases by membrane gas absorption, *Journal of Nanjing University of Technology*, **31**, 96-101.

Lv Y.X., Yu X.H., Tu S.D. and Yan J. (2012), Experimental studies on simultaneous removal of CO_2 and SO_2 in a polypropylene hollow fiber membrane contactor, *Applied Energy*, **97**, 283-288.

Marzouk S.A.M. and Al-Marzouqi M.H. (2010), Gas analyzer for continuous monitoring of carbon dioxide in gas streams, *Sensors and Actuators B: Chemical*, **145**, 398-404.

Marzouk S.A.M., Al-Marzouqi M.H., El-Naas M.H. and Ismail Z.M. (2010a), Removal of carbon dioxide from pressurized CO_2-CH_4 gas mixture using hollow fiber membrane contactors, *Journal of Membrane Science,* **351**, 21-27.

Mavrotas G., Pavlidou S., Hondou V. and Diakoulaki D. (2000), Decomposition analysis of CO_2 emissions from the greek manufacturing sector, *Global NEST Journal*, **2**, 119-127.

Mavroudi M., Kaldis S.P. and Sakellaropoulos G.P. (2006), A study of mass transfer resistance in membrane gas–liquid contacting processes, *Journal of Membrane Science,* **272**, 103-115.

Nyambura M.G., Mugera G.W., Felicia P.L. and Gathura N.P. (2011), Carbonation of brine impacted fractionated coal fly ash: Implications for CO_2 sequestration, *Journal of Environmental Management*, **92**, 655-664.,

Ozturk B. and Hughes R. (2012), Evaluation of Mass Transfer characteristics of non-porous and microporous membrane contactors for the removal of CO_2, *Chemical Engineering Jounal,* **195-196**, 122-131.

Pan S.Y., Chang E.E. and Chiang P.C. (2012), CO_2 capture by accelerated carbonation of alkaline wastes: A review on its principles and applications, *Aerosol and Air Quality Research*, **12**, 770-791.

Paul S., Ghoshal A.K. and Mandal B. (2008), Theoretical studies on separation of CO_2 by single and blended aqueous alkanolamine solvents in flat sheet membrane contactor (FSMC), *Chemical Engineering Journal,* **144**, 352-360.

Prasad R. and Sirkar K.K. (1988), Dispersion-free solvent extraction with microporous hollow-fiber modules, *AIChE Journal*, **34**, 177-188.

Rahbari-Sisakht M., Ismail A.F. and Matsuura T. (2012), Development of asymmetric polysulfone hollow fiber membrane contactor for CO_2 absorption, *Separation and Purification Technology*, **86**, 215-220.

Rahbari-Sisakht M., Ismail A.F., Rana D. and Matsuura T. (2012a), Effect of novel surface modifying macromolecules on morphology and performance of polysulfone hollow fiber membrane contactor for CO_2 absorption, *Separation and Purification Technology*, **99**, 61-68.

Rahbari-Sisakht M., Ismail A.F., Rana D. and Matsuura T. (2012b), A novel surface modified polyvinylidene fluoride hollow fiber membrane contactor for CO_2 absorption, *Journal of Membrane Science*, **415-416**, 221-228.

Rajabzadeh S., Yoshimoto S., Teramoto M., Al-Marzouqi M. and Matsuyama H. (2009), CO_2 absorption by using PVDF hollow fiber membrane contactors with various membrane structures, *Separation and Purification Technology*, **69**, 210-220.

Rajabzadeh S., Yoshimoto S., Teramoto M., Al-Marzouqi M., Ohmukai Y., Maruyama T. and Matsuyama H. (2013), Effect of membrane structure on gas absorption performance and long-term stability of membrane contactors, *Separation and Purification Technology*, **108**, 65-73.

Rezakazemi M., Niazi Z., Mirfendereski M., Shirazian S., Mohammadi T. and Pak A. (2011), CFD simulation of natural gas sweetening in a gas–liquid hollow-fiber membrane contactor, *Chemical Engineering Journal*, **168**, 1217-1226.

Shirazian S., Moghadassi A. and Moradi S. (2009), Numerical simulation of mass transfer in gas–liquid hollow fiber membrane contactors for laminar flow conditions, *Simulation Modeling Practice and Theory*, **17**, 708-718.

Sridhar S., Smitha B. and Aminabhavi T.M. (2007), Separation of carbon dioxide from natural gas mixtures through polymeric membranes - A review, *Separation and Purification Reviews*, **36**, 113-174.

Sun C.G., Cao Y.M., Jie X.M., Wang T.H., Lin B. and Yuan Q. (2007), Mass transfer mechanism of CO_2 absorption through a non-porous hollow fiber contactor, *Journal of Chemical Engineering of Chinese Universities*, **21**, 556-562.

Sun C.G., Cao Y.M., Zuo L., Lin B., Jie X.M. and Yuan Q. (2005), Mass transfer mechanism of CO_2 absorption through a non-porous hollow fiber contactor, *Chemical Journal of Chinese Universities*, **26**, 2097-2102.

Sun, C.G. (2005), Study on non-porous hollow fiber contactors for CO_2 removal, M.S. Thesis, Chinese Academy of Sciences.

Thanedgunbaworn R., Jiraratananon R. and Nguyen M.H. (2007), Shell-side mass transfer of hollow fibre modules in osmotic distillation process, *Journal of Membrane Science,* **290**, 105-113.

Versteeg G.F., Van Dijck L.A.J. and Van Swaaij W.P.M. (1996), On the kinetics between CO_2 and alkanolamines both in aqueous and non-aqueous solutions: An overview, *Chemical Engineering Communications*, **144**, 113-157.

Viegas R.M.C., Luque S., Alvarez J.R., Coelhoso I.M., Crespo J.P.S.G. and Rodriguez M. (1998), Mass transfer correlations in membrane extraction: Analysis of Wilson-plot methodology, *Journal of Membrane Science*, **145**, 129-142.

Wang K.L. and Cussler E.L. (1993), Baffled membrane modules made with hollow fiber fabric, *Journal of Membrane Science,* **85**, 265-278.

Wang Q.H., Zhang W.F., Fang M.X., Luo Z.Y. and Cen K.F. (2009), Separation of CO_2 in flue gas by membrane absorption in China, *Environmental Science and Technology*, **32**, 68-74.

Wang R., Li D.F. and Liang D.T. (2004), Modeling of CO_2 capture by three typical amine solutions in hollow fiber membrane contactors, *Chemical Engineering and Processing*, **43**, 849-856.

Wongchitphimon S., Wang R. and Jiraratananon R. (2011), Surface modification of polyvinylidene fluoride-co-hexafluoropropylene (PVDF–HFP) hollow fiber mmembrane for membrane gas absorption, *Journal of Membrane Science,* **381**, 183-191.

Wu, J. and Chen, V. (2000), Shell–side mass transfer performance of randomly packed hollow fiber modules, *Journal of Membrane Science,* **172**, 59-74.

Yan Y.F., Zhang Z.E., Zhang L. and Ju S.X. (2014), Research progress in hollow fiber membranes for CO$_2$ capture, *Natural Gas Industry*, **34**, 114-123.

Yang M.C. and Cussler E.L. (1986), Designing hollow-fiber contactors, *AIChE Journal*, **32**, 1910-1916.

Yang M.F, Fang M.X., Zhang W.F., Wang S.Y., Xu Z.K., Luo Z.Y. and Cen K.F. (2005), Removal of CO$_2$ from simulated flue gas of power plants by membrane-based gas absorption processes, *Environmental Science*, **26**, 24-29.

Yang Q., Bown M., Ali A., Winkler D., Puxty G. and Attalla M. (2009), A carbon-13 NMR study of carbon dioxide absorption and desorption with aqueous amine solutions, *Energy Procedia*, **1**, 955-962.

Yuan W.F., Zhang W.F., Wang S.Y., Fang M.X., Xu Z.K., Luo Z.Y. and Cen K.F. (2004), CO$_2$ separation from flue gases by polypropylene hollow fiber membrane contactor, *Energy Engineering*, **4**, 9-12.

Zhang C.J., Yin Y.H., Zhou X., Zhou J.C. and Gong J.S. (2010), Study on influenced factors of low concentration CO$_2$ removal by hollow fiber membrane contactor, *Ship Science and Technology*, **32**, 91-96.

Zhang H.Y., Wang R., Liang D.T. and Tay J.H. (2008), Theoretical and experimental studies of membrane wetting in the membrane gas–liquid contacting process for CO$_2$ absorption, *Journal of Membrane Science,* **308**, 162-170.

Zhang L.Z., Huang S.M., Chi J.H. and Pei L.X. (2012), Conjugate heat and mass transfer in a hollow fiber membrane module for liquid desiccant air dehumidification: A free surface model approach, *International Journal of Heat and Mass Transfer*, **55**, 3789-3799.

Zhang Q. and Cussler E.L. (2004), Hollow fiber gas membranes, *AIChE Journal*, **31**, 1548-1553.

Zhang W.F., Fang M.X., Yan S.P., Wang J.L., Luo Z.Y. and Cen K.F. (2007), Comparison of dissociation performance of CO$_2$ from flue gas by hollow fiber membrane contactors, *Journal of Power Engineering*, **27**, 606-610.

Zhang W.F., Wang Q.H., Fang M.X., Luo Z.Y. and Cen K.F. (2008), Progress of separation of CO$_2$ from flue gas by membrane absorption, *Chemical Industry and Engineering Progress*, **27**, 635-639.

Zhang Y., Zhang J., Liu B.C., Wu H.C. and Li Q.L. (2010), Experimental comparison the performance between mixed alcohol amine and MEA absorption method in CO$_2$ absorption from the power plant flue gas, *Chemical Industry and Engineering Progress*, **29**, 435-438.

Zhang Y.P., Jiang J.Z., Ji Q.Q. and Luo H.Q. (2012), Research on CO$_2$ absorption of flue gas in the mixed alcohol amine solutions, *Chemical Production and Technology*, **19**, 22-24.

Zhang, W.F. (2006), Experimental Study on Separation Carbon Dioxide from Flue Gases Using Hollow Fiber Membrane Contactor, Ph.D. Thesis, Department of Energy Engineering, Zhejiang University.

Zheng J.M., Dai Z.W., Wong F.S. and Xu Z.K. (2005), Shell side mass transfer in a transverse flow hollow fiber membrane contactor, *Journal of Membrane Science*, **261**, 114-120.

Zheng J.M., Xu Z.K., Li J.M., Wang S.Y. and Xu Y.Y. (2004), Influence of random arrangement of hollow fiber membranes on shell side mass transfer performance: a novel model prediction, *Journal of Membrane Science*, **236**, 145-151.

Zhu B.K., Chen W., Wang J.L., Xu Y.Y. and Xu Z.K. (2003), Separation of carbon dioxide from gas mixture by membrane contactor, *Environmental Science*, **24**, 34-38.