HOLLOW FIBER MEMBRANE ABSORPTION OF CO\(_2\) IN THE FLUE GAS

YAN YUNFEI\(^1\), ZHANG ZHIEN\(^1\), ZHANG LI\(^1\), and JU SHUNXIANG\(^1\)

\(^1\)Key Laboratory of Low-grade Energy Utilization Technologies and Systems, China, 40044, \(^2\)College of Power Engineering, Chongqing University, China, 40044
e-mail: yunfeiyan@yahoo.com.cn

EXTENDED ABSTRACT

With the aggravation of greenhouse effect, the emission control of greenhouse gases which mainly consists of CO\(_2\) has caught close attention by the global researchers. Compared with traditional absorption methods, hollow fiber membrane absorption of CO\(_2\) in flue gas is a removal method of high efficient and has a promising prospect. In this paper, based on the fundamentals and characteristics of membrane absorption process, the development and the status from the membrane materials, membrane structure, absorbents, etc. have been reviewed; the characteristics of absorbent are summarized in detail, and the effects of absorption process on the gas phase flow and pressure, the liquid flow and pressure, etc. are also analyzed. Furthermore, several existing issues in this area are suggested, and the future application is prospected.

**Keywords:** hollow fiber membrane, absorption, flue gas, carbon dioxide, mass transfer

1. INTRODUCTION

Recently, with the aggravation of greenhouse effect, the emission control of greenhouse gases which mainly consists of CO\(_2\) has caught close attention by the global researchers [1]. Fossils fuels such as petroleum, natural gas and coal are still the major sources of energy throughout the world. A substantial growth of CO\(_2\) emissions in the past 150 years has resulted in significant increasing of atmospheric CO\(_2\) concentration, which caused the global average temperature rising 5.3°C obviously [2]. As the second-largest economy, the CO\(_2\) emissions in China overtook America in 2007 leaping to first in the world for the first time because of the increasing demand in energy. Currently owing to the problems of resources, history, technology, etc. the coal consumption accounts for about 75% of total domestic energy consumption, and coal will be the main raw material lasting for at least 50 years [3]. Therefore, dealing with the large amount of CO\(_2\) of tail gas from the coal fired power plant is extremely urgent and particularly important.

Nowadays there are several separation methods of CO\(_2\) absorption from industrial flue gas, including absorption, adsorption, membrane separation and cryogenic distillation, etc[4]. The purity of CO\(_2\) using absorption is as high as above 99.9%, meanwhile this technology is mature, while membrane separation saves more energy. So membrane gas absorption (MGA) coupling technology which combines membrane gas separation and chemical absorption has been paid much attention due to its advantages in gas-liquid contact area, mass transfer rate, no entrainment, elasticity of operation and equipment size[5]. Relative to other traditional separation methods, membrane absorption is a kind of method with high efficiency and low cost [6-7]. Among them, the hollow fiber membrane contactor has been widely used due to the characteristics of high absorption efficiency, small volume, light weight and low cost [8-9]. But it is still not found the absorbent that has high CO\(_2\) absorption and desorption properties, and not clear how the factors influence absorption-desorption process mechanism. Therefore, the fundamentals of membrane absorption and the factors of absorption process and mass transfer process are summarized in this paper. Furthermore, an experimental program of high efficient hollow fiber membrane absorption and desorption of CO\(_2\) is proposed.
2. FUNDAMENTALSMICROSCALE MODEL DESCRIPTION
The method of membrane absorption is a new way that combines the membrane separation and conventional absorption, mainly using pore membrane. Driving force of this technology to realize the gas separation is the interaction concentration gradient. The mass transfer process includes three steps: (1) the solute is transmitted from the gas phase to the membrane surface; (2) the solute is transmitted to the gas-liquid interface through the membrane pores; (3) finally the solute is absorbed into the liquid phase by absorbent from gas-liquid interface [10].

In the membrane absorption method Gas and absorbent contact indirectly, and the gas-liquid interface is fixed, moreover they separately flow on both sides. The membrane itself does not have the selectivity to the gas, only functions as separating gas and absorbent, meanwhile CO₂ is diffused to the liquid phase side through the membrane driving by the concentration gradient. Theoretically the separated gas is easily penetrated to another side of the membrane under low pressure through the membrane pore, mainly depending upon the selective absorption of absorbent to achieve the goal of separation the gas mixture [11-12]. The fundamental is showed in Figure 1.

3. ANALYSIS of PROCESS INFLUENCE FACTORS
3.1. MEMBRANCE MATERIALS
There are three main membrane material types including organic polymer membrane, inorganic membrane and organic-inorganic composite membrane. Especially polythene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF), polytetrafluorethylene (PTFE), polysulphone (PS) and polyethersulfone (PES) are widely used in membrane manufacture. The hydrophobic membrane materials are currently used which has bigger contact area than hydrophilic membrane materials, and in such absorption process the membrane pores are filled with the gas. The membrane materials that hollow fiber membrane module uses are different; particularly PP membrane is massively applied in the industry because of its low cost. Moreover PTFE membrane has advantages in good mechanical properties and self-lubricating quality, high-temperature resistant, anti-chemical erosion compare with other membrane materials.

Cheng et al. [13] investigated the carbonic anhydrase hollow fiber membrane contactor removal CO₂ in the enclosed space, and found that the composite membrane had both
advantages of the cellulose acetate membrane and PP membrane, at meantime improving the CO$_2$ removal rate and reducing the CO$_2$ content in feed gas from 0.52% to above 0.09%. Wang et al. [14] developed a polyethylene amine-poly sulfone (PVAm-PS) composite membrane having high absorption capacity to CO$_2$, and little absorption to N$_2$, H$_2$ and CH$_4$, therefore. This membrane has high selective permeability to CO$_2$. The absorption capacity of composite membrane is mostly from the PVAm composite layer, while the absorption capacity is mainly from a large number of primary amine groups. Rahbawi-Sisakht group [15-18] successively found that surface modified membrane contactor had higher critical water inlet pressure and CO$_2$ absorption efficiency under the same conditions, comparing with physical and chemical absorption CO$_2$ in use of ordinary PS hollow fiber membrane contactor. At the same time using PVDF hollow fiber membrane verified the results.

By using the polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) composite membrane with NaOH aqueous solution absorption of CO$_2$, Wongchitphimon et al. [19] observed that the liquid inlet pressure and contact angle increased by 36% and 33% respectively, and the total mass transfer coefficient rose from 5.69×10$^{-5}$ m·s$^{-1}$ to 7.56×10$^{-5}$ m·s$^{-1}$ relative to a single membrane. Ma et al. [20] composed 1.0-3.0 dendritic polymer polyamide-amine (PAMAM) through divergent approach, which could be used for coating on the layer of polyimide/polymer polyamide-amine (PI/PAMAM) composite membrane, investigated the influence of PAMAM algebra to the permeability of pure CO$_2$, N$_2$ in the composite membrane and the performance on CO$_2$/N$_2$ separation. The results indicated that when the 3.0 PAMAM was experimented, the CO$_2$ permeability coefficient was up to 106.6 Barrer and CO$_2$/N$_2$ separation coefficient was reached 44.25. Khaisri et al. [21] studied three kinds of membrane materials (PE, PTFE and PVDF) and MEA solution separately absorption CO$_2$ in the gas mixture, finding that their stability order were PTFE>PVDF>PP.  

3.2. CONNECTION FORM OF MEMBRANCE MODULE 
A single, serial and parallel membrane modules are usually used in research. Zhang et al. [22] found the forms in series or parallel performed better owing to bigger absorption area. At the same time serial way was better than parallel way because of advancement in absorption stroke and the gas-liquid contact time. In the model study on the effects of membrane module arrangement, Boributh et al. [23] compared with these three models, also found that the serial form had the best absorption performance.

3.3. MEMBRANCE STRUCTURE 
The choice of absorbent needs to consider the factors including its absorption ability, regeneration ability and energy consumption, etc.; and physical parameters including absorbent viscosity, surface tension, good compatibility with membrane materials, good thermal stability, etc. These are all important factors influencing membrane absorption process’s mass transfer, heat transfer and reaction.

Absorbent adopted by researchers at home and abroad has been developed from the original H$_2$O, alkali solutions, inorganic salts, traditional alcohol amine solution to containing additive or composite absorbent. According to a large number of experimental studies on membrane absorption CO$_2$ in the mixed gases by Al-Marzouqi et al. [30], it has been found that the separation efficiency sequences of absorbents were TEPA>TETA>DETA>EDA>MEA>DEA, DETA>MEA>DEA>MDEA. CO$_2$ in flue gas was separated and simulated by using hydrophobic PVDF hollow fiber membrane by Lai et al. [31]. The effects of the different absorbent separation performance was NaOH>GLY>H$_2$O. And when the liquid concentration and flow rate improving, separation efficiency increased; when gas flow rate and CO$_2$ concentration increasing, it decreased. It has been found that separation efficiency sequence is NaOH>TEA>MEA>DEA>H$_2$O,
when Cao et al. [32] used hollow fiber membrane to absorb CO₂ to compare the removal rate. Especially when using 2×10³ mol·m⁻³ NaOH, the absorption effect was close to natural penetration. The experimental study for simulation flue gas by Zhang et al. [22,33,34] showed that the absorption effect was NaOH>MEA>DEA>TEA. At the same time reducing the energy consumption to require absorbent efficient recycling usage, it has been found on trial that desorption effect was GLY>MEA>MDEA. In addition GLY desorption was the most difficult and MDEA absorption capacity was big, meanwhile desorption effect was best. the study of Yang et al. [35] using alcohol amine solution absorption and desorption CO₂ also found that desorption efficiency was MEA<MMEA<MDEA. In the study of a single absorbent absorbing CO₂ regeneration performance, Yan [36] reported that absorbent regeneration order was TEA=MDEA>AMP>DEA>DIPA>PZ>MEA. Chonqing University Zhang's group [37-41] quoted pH value oscillating method to analyze reaction mechanism of alcohol amine solution absorption and desorption CO₂. The system process indicated that in the same experiment conditions, the absorption rate of MEA was highest and desorption rate of MDEA was highest. It could be concluded that the absorption and desorption characteristics of mixed amine solution was better than single amine.

Table 1 described the absorption and desorption performance of absorbents used by researchers at home and abroad. The CO₂ absorption performance order is NaOH>TEPA>TETA>DETA>GLY>MEA>DEA>DIPA>AMP>TEA>MDEA→K₂CO₃→H₂O; comprehensive CO₂ regeneration performance order is TEA=MDEA>DEA>AMP>DIPA>MEA>NaOH.

<table>
<thead>
<tr>
<th>Absorbability</th>
<th>Types</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bases (NaOH, KOH, etc.)</td>
<td>Rapid absorption. High absorption capacity. High rate of removal</td>
<td>High price. Unregenerated</td>
</tr>
<tr>
<td>2</td>
<td>GLY</td>
<td>Rapid absorption. High absorption capacity. High rate of removal, Hard to wet the fenestra</td>
<td>Regeneration more difficult than Alkanolamine solution</td>
</tr>
<tr>
<td>3</td>
<td>MEA</td>
<td>Rapid absorption. Low price. Rarely Absorbing hydrocarbon</td>
<td>Low absorption capacity, Corrosivity. High heat capacity. high energy consumption of desorption</td>
</tr>
<tr>
<td>4</td>
<td>DEA</td>
<td>Rapid absorption. Low heat capacity</td>
<td>Low absorption capacity. Corrosivity</td>
</tr>
<tr>
<td>5</td>
<td>DIPA</td>
<td>Rapid absorption. High absorption capacity. Good stripping features</td>
<td>High heat capacity, high energy consumption of desorption</td>
</tr>
<tr>
<td>6</td>
<td>AMP</td>
<td>High absorption capacity. Low heat capacity. Little corrosivity. Good stripping features, easy to regeneration</td>
<td>Slow absorption</td>
</tr>
</tbody>
</table>

Note: GLY-amino acid potassium; MEA-ethanol amine; DEA-diethanol amine; DIPA-disopropanol amine; AMP-steric hindered amine; TEA-trithanolamine; MDEA-methyl diethanolamine; EDA-ethene diamine; DETA-diethylentriamine; TETA-Ethanediamine; TEPA-tetraethylene pentamine; MMEA-methylmonooctanalamine; PG-ammonia potassium acetate; PZ-piperazidine.

In addition, because a single absorbent cannot completely meet the high regeneration performance and high absorption rate, the researches not only limits in one absorbent, but also in mixed absorbents. Commonly used activator are alicyclic amine, alcohol amine and enamine, etc. Lin et al. [42] used AMP and activator PZ, found that with increase of additive concentration, CO₂ absorption rate constantly improved. Zhang et al. [43] investigated that mixed alcohol amine solution absorption of CO₂ in flue gas was the
performance of the hybrid system, the study found that the activation effect of MDEA for
CO2 absorption rate and absorbed dose was MDEA/DETA>MDEA/PZ>MDEA/MEA, namely diethylene diamine was best, while ethanolamine was worst. Under the same
conditions, Zhang et al. [44] adopted some mixed alcohol amine solutions studying the
absorption rate on the experiment, and found that mixed amine MEA/AMP performed
well, whereas mixed amine MEA/TEA absorption effect was poorer, Paul [45] also got the
same results. By performing the absorption and regeneration characteristics of different
proportion of the mixed absorbent for research, Yan [36] finally reported that adding
quantity activator into tertiary amine showed the best performance. The normal
membrane absorption test conditions and parameters were summarized in Table 2. In
collection, MEA/TEA, MEA/MDEA, MEA/AMP, PZ/TEA, PZ/MDEA, PZ/AMP and
PZ/DEA etc. showed good comprehensive performance. Therefore, it has better
absorption and regeneration comprehensive performance of using mixed absorbent
which has high absorption rate and high regeneration performance. So in practical
industrial application, appropriate adjustments should be adopted according to the actual
situation, the optimal activator types and concentration should be decided to achieve the
best absorption effect, then it is necessary for finding one absorbent of high efficient
absorption and regeneration.

### Table 2. Under different conditions of membrane absorption experiments.

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Absorbents</th>
<th>Flue gas component</th>
<th>Membrane Materials</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chen, etc.</td>
<td>AMP/MEA/PZ</td>
<td>1-9.5%CO2, 90.5-99%N2</td>
<td>PTFE</td>
<td>[24,46]</td>
</tr>
<tr>
<td>Lin, etc.</td>
<td>MDEA/PZ, AMP/PZ</td>
<td>1-15%CO2, N2</td>
<td>PVDF, PP</td>
<td>[41,47,48]</td>
</tr>
<tr>
<td>Lv, etc.</td>
<td>Delonized water, MEA, MDEA</td>
<td>40% CO2, 60%N2</td>
<td>PP</td>
<td>[49,50]</td>
</tr>
<tr>
<td>Zhang, etc.</td>
<td>MEA, PG</td>
<td>CO2 (≤5.0%)</td>
<td>PP</td>
<td>[29]</td>
</tr>
<tr>
<td>Al-Marzouqi, Faiz, etc.</td>
<td>K2CO3</td>
<td>5%CO2, 5%H2S, 90%CH4</td>
<td>PP</td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td>MEA,NaOH</td>
<td>10% CO2, 90%CH4</td>
<td>PP</td>
<td>[52,53,54]</td>
</tr>
<tr>
<td></td>
<td>MEA</td>
<td>10%CO2, 10%H2S, 80%CH4</td>
<td>PVDF, PP</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>MEA</td>
<td>Pure CO2</td>
<td>PVDF</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>NaOH, TETA, MEA, MDEA</td>
<td>2%H2S, 98%CH4</td>
<td>PTFE</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td>H2O, NaOH, MEA, DEA, TETA</td>
<td>9.5%CO2, 90.5%CH4</td>
<td>PTFE</td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td>MEA, DEA, EDA, TEPA, TETA, DETA</td>
<td>10% CO2, 90%CH4</td>
<td>PP,SR</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td>DETA, DAE, DEYA, BEHA</td>
<td>5% CO2, 95%CH4</td>
<td>PVDF</td>
<td>[58]</td>
</tr>
<tr>
<td>Khaisri, deMontigny, etc.</td>
<td>MEA</td>
<td>Pure CO2</td>
<td>PTFE</td>
<td>[59,60,61]</td>
</tr>
<tr>
<td></td>
<td>MEA, AMP</td>
<td>15%CO2, 85%air</td>
<td>PTFE, PP</td>
<td>[21,27]</td>
</tr>
<tr>
<td>Cao, etc.</td>
<td>NaOH, MEA, DEA, TEA</td>
<td>Pure CO2</td>
<td>PS, SR</td>
<td>[32,62]</td>
</tr>
<tr>
<td></td>
<td>Salt water, Fresh water</td>
<td>25%CO2, 75%N2</td>
<td>Pi</td>
<td>[63]</td>
</tr>
</tbody>
</table>

### 4. CONCLUSIONS

With the increasing greenhouse effect, reducing carbon emission is globally urgent.
Although membrane absorption method has a good prospect to reduce pollutants
emissions in the power plant, for example, using this method for removing SO2, H2S, NH3
and other acidic gas from the flue gas of coal or gas power plant, but it is difficult to apply
it in a large-scale commerce because of existing many technical and economic difficulties
needed to be solved urgently. The main problems of membrane gas absorption focus on
the following aspects:

(1) The operation cost of membrane absorption. Absorbent should have a good removal
effect and regeneration performance, which is cheap and easy to recycle. The research
should be focused on research to reduce energy consumption in desorption which will
decrease the operating cost. Meanwhile, the new membrane materials should be
developed, which can be high temperature resistant, corrosion resistant, easy cleaning,
pollution resistant. We can also look for breakthroughs from inorganic membrane and

CEST2013_0698
metal membrane. It is important to develop one material which has high quality and low price, strong hydrophobicity, high stability and thin layer. The main point is to improve the selectivity and permeability of membrane in the following researches.

(2) Source of Flue gas. At present, the raw gas is mainly made by several pure gas in the membrane absorption CO\textsubscript{2} experiments. Few scholars use the real flue gas in experiments. It is because the real flue gas contains other gas, like SO\textsubscript{x}, H\textsubscript{2}S, CH\textsubscript{4}, and some solid dust. In addition, the high temperature will influence experimental results. Therefore, we should consider more comprehensive interference factors in order to keep in line with the actual plant conditions in future.

(3) Simulation of membrane absorption process. We should constantly optimize the mass transfer model of membrane absorption process because the material and structure of membrane module, and absorption is different. We should further analyze thermodynamic process of reaction between new absorption solution and CO\textsubscript{2}, so as to get the best operating parameters and conditions to achieve the purpose of improving the efficiency of absorption.

(4) Evaluation the economy of membrane absorption CO\textsubscript{2}. Currently, there is a lack of detailed economic evaluation and analysis method about membrane absorption process. We need to further investigate on decarbonization system of every power plant in our country, to study the factors of absorption effect due to different coaly types and power plant scales. Thereby we can achieve the best technological process and receive optimum operating parameters.

ACKNOWLEDGMENT
The authors were supported by the Fundamental research funds for the Central Universities (No.CDZR12140034).

REFERENCES


