Carbon Dioxide Removal in a Membrane Contactor – Selection of Absorptive Liquid/Membrane System

Anna Witek-Krowiak, Anna Dawiec, Szymon Modelski, and Daria Podstawczyk

Abstract—This report demonstrates the application of the membrane contactor for carbon dioxide removal. The investigations were performed with the use of a single polypropylene capillary membrane. Two primary amines (monoethanolamine MEA, diglycolamine DGA), one secondary amine (diethanolamine DEA), one tertiary amine (methyl-diethanolamine MDEA) were used to prepare absorbate solutions. Batch experiments were conducted for the counter-current flow with liquid on the tube side of the module. The system was investigated for aqueous solutions of amines and for the solutions with piperazine addition. The absorption kinetics with the use of primary amines appeared to be much faster than those of secondary and tertiary amines. The amine efficiency can be stated as follows: MEA>DGA>DEA>MDEA. Further investigations have shown that the presence of an activator improves the reaction and process kinetics and brings the DEA and MDEA efficiency to the level of primary amines. The influence of different types of amine solutions used as liquid absorbents on the stability of the membrane shows that these solutions do not wet PP (polypropylene) membranes even after 150 days’ immersion in different absorbents.

Index Terms—Amines, carbon dioxide, membrane absorption, membrane contactors.

I. INTRODUCTION

Membrane contactors are hybrid combinations of advanced membrane techniques with an effective absorption process. The hybrid system concept is the newest solution in the field of industrial absorption. Membrane contactors are a novel type of hybrid mass exchangers, where a porous membrane separates two phases (Fig. 1.). In membrane absorbers, the selective sorbent performs the separatory function, while the membrane facilitates the mass exchange process by expanding the phase contact surface area [1, 2]. Membranes with modified surface properties may improve the selectivity of the process by selectively inhibiting the transport of one of the mixture constituents. Compared to the traditional column device, membranes allow for a 4-5-fold increase in yield per apparatus unit volume. Since the sorptive liquid flows within capillaries and both phases are not directly contacting each other, membrane absorbers may operate in any spatial configuration (horizontal, vertical) and at any flux ratios between both phases. Contrary to packed columns, there is a possibility for a large amount of gas to contact a small amount of liquid – there is no flooding or uneven packing moisturization. The apparatus operates with unchanging yields, regardless of their diameter and height (length), which is particularly important when scaling up the device. Thanks to the sectional design, scaling up amounts simply to multiplication of the number of modules. Membrane contactors make use of affordable micro- and ultrafiltration membranes, manufactured on a large scale from various polymer and ceramic materials. Membranes may also play an active role by limiting the contact of undesirable components (such as NOx and SOx) with the sorptive liquid, thus extending its lifespan. Another advantage of membrane contactors that results from separation of individual process streams is the possibility of carrying out several unit processes in a single apparatus, which becomes particularly interesting in cases when one of such processes is exothermic, and the other is endothermic. This presents an opportunity for an energetic balance of the process or for waste heat utilization.

Membranes in membrane gas/liquid contactors are generally hydrophobic [3, 4], prepared from polymer materials like polypropylene (PP), polyethylene (PE), polysulphone (PS), polyethersulfone (PES), poly(vinylidene fluoride) (PVDF) and polytetrafluorethylene (PTFE). Hydrophobic ceramic materials could be applied in this process as well. Additionally, hydrophobic surface modification can improve non-wettable properties of the membrane.

Selection of proper liquid absorbent for removal of CO2 in the membrane contactor should be based on physicochemical properties of the liquid and the influence of the solvent on the membrane properties. The most important factors for sorbent selection are sorption capacity of the absorbent, solvent stability, surface tension of the absorbent (wetting characteristics), viscosity of the absorptive liquid, chemical compatibility with the material of the membrane, low vapor

Fig. 1. Concentration profile in a membrane contactor.

DOI: 10.7763/IJCEA.2012.V3.225
pressure, facility of regeneration.

The aim of this study was to investigate the membrane absorption of CO₂ using amine solutions and the influence of the activator presence (piperazine) in the solution on the effectiveness of the absorption process. Further, we have investigated the interaction between the absorbents and membranes. PP fibers were immersed in different absorbents up to 150 days.

II. MATERIALS AND METHODS

A. Membrane and Absorbers

In this study polypropylene (PP) membrane was used. The membrane has a length of 0.2 m, an internal diameter of 1.8 mm, and an external diameter of 2.4 mm. The membrane was placed in a glass cover with an internal diameter of 0.02 m. A liquid was poured into the internal part of the membrane, and a gas was directed into the shell side of the membrane in the counter-current mode.

The study was conducted at a high molar ratio of amine to the carbon dioxide in the system, allowing for a negligible change in the concentration of amines during the process. The rate of change in the concentration during the process depends mainly on the chemical reaction kinetics of carbon dioxide with amine, which makes possible to identify the best absorbent. The initial concentration of CO₂ was 5% [v/v].

Monoethanolamine (MEA), diethanolamine (DEA) supplied by POCH®, diglycolamine (DGA), methyldiethanolamine (MDEA), piperazine (P) supplied by Sigma-Aldrich® were dissolved in deionized water to prepare single and blended absorptive solutions.

B. CO₂ Absorption in a Membrane Contactor

A gas/liquid membrane contactor was used to determine the mass transfer coefficients of CO₂ absorption. Experiments were conducted in a gas-liquid membrane contactor (Fig. 2). Feed gas (5% CO₂ in N₂) was introduced to the shell side of the membrane module with a flow rate of 6400 ml/min. Liquid flowed through the lumen side of the membrane with a flow rate of 230 ml/min. The gas side pressure was set at an atmospheric value; the liquid side pressure was set at 0.2 bar. All experiments were carried out at room temperature (20°C). The gases coming from the absorption were sampled and analyzed by FT-IR Nicolet 380 (Thermo Scientific).

C. Long-Term Stability of the Membrane Experiments

30 mm long pieces of the membrane were immersed into the absorptive liquids (5 fibers in each absorbent). It was assumed that the immersed PP fibers would undergo similar exposure conditions as those used in hollow fiber membrane contactors. After a specific period of time (5, 20, 50, 90, 150 days), the fibers were taken out, washed with distilled water and dried. The contact angle measurements were conducted to control the membrane hydrophobicity, using microscope Janamed 2 Fluorescence. A droplet of proper liquid was placed on the surface of the membrane. A contact angle was calculated from a digital image of the liquid drop placed on the membrane surface [5, 6]. Measurements were repeated threefold and an average value was selected.

III. RESULTS AND DISCUSSION

A. CO₂ Absorption in a Membrane Contactor

Experiments were carried out to determine a degree of carbon dioxide absorption during the process for the solutions of amines without addition of piperazine. Obtained results show that the membrane absorption runs preferably for primary amines MEA and DGA (Fig. 1A). The absorption for the secondary and tertiary amine (DEA and MDEA) solutions goes at a slower rate.

For the process time of 10 min, the degree of absorption for primary amines was over 60%, for the secondary and tertiary amine the degree of absorption doesn’t exceed 20%. These results are concurrent with the previous findings [7]. In order to increase the rate of the reaction of carbon dioxide with an amine, an activator – piperazine - was introduced to the system. It was observed that the addition of piperazine strongly enhances the absorption in the case of secondary and tertiary amines, and slightly in the case of primary amines (Fig. 1B).

B. Mass Transfer Coefficients in the Presence of the Activator

The membrane absorption process is driven by the absorbate concentration/pressure difference. According to the well established “resistance in series” model, the overall mass transfer coefficient consists of individual resistances. Following the absorbate concentration gradient, the convective-diffusive transport occurs from the bulk of the gas phase to the membrane surface, after which absorbate molecules diffuse through the pores of the membrane (diffusion in gas phase - dry mode, diffusion in gas and liquid - partially wet mode, diffusion in liquid phase - wet mode) and then convective-diffusive transport from the membrane surface to the bulk of the liquid occurs. The convective-diffusive transport on the gas and liquid side is conventionally reduced to the bulk phase and a thin diffusive film (diffusive film theory). At the gas/liquid interface an absorbate concentration discontinuity exists arising from physicochemical equilibrium. This equilibrium is usually linear in low concentration regions, hence such regions are described with Henry’s Law. The absorbate flux continuity is kept by introducing the equilibrium constant into flux equations for gas, membrane and liquid [8]. Summarizing flux equations, the following equation can be written for...
unsteady transport of absorbate from the bulk of the gas to the bulk of the liquid [1]:

\[ \frac{\partial c_x}{\partial t} = -w_x \frac{\partial c_x}{\partial z} - K_x (c_x - c, H) \]  
(1)

\[ \frac{1}{K_x} = \frac{1}{k_x} \frac{1}{k_m} + \frac{H}{k_l} \]  
(2)

(3)

The above equations are correct for the physical absorption processes. Many of absorption processes are carried out with the use of reactive solutions to improve their efficiency. The common practice is the use of alkaline or amine solutions in the gas sweetening process, sulfur oxides removal etc. A potential usage of membrane contactor for the carbon dioxide absorption is based on the amine sorbents, so the model must be adequately modified. To introduce reactive effects that improve the absorption rate, the so called "enhancement factor", \( E \) is applied. The factor describes by equation (1) with the following assumptions being made for further calculations:

1) The absorbate concentration profile along the module is negligible (high flow rates and short module);
2) The gas side mass transfer resistance is negligible (high flow rate);
3) The amine concentration change during experiment is negligible (very high molar CO2/amine ratio);
4) The convective-diffusive transport resistance on the liquid side is negligible;
5) The membrane absorber works in a dry mode.

On the basis of above assumptions the flux equation (1) reduces to:

\[ \frac{\partial c_x}{\partial t} = -K_x c_x \]  
(4)

for the constant gas volume of the batch system the above equation can be rearranged to:

\[ V_x \frac{\partial c_x}{\partial t} = -K_x a c_x \]  
(5)

and the overall mass transfer coefficient is comprised of membrane and liquid side mass transfer resistance:

\[ \frac{1}{K_x} = \frac{1}{k_x m} + \frac{H}{k_l} \]  
(6)

The in-time gas concentration measurements were fitted with the presented equation to obtain the \( K_x \) value (Fig. 4). To check the reproducibility, the experiments for each set of conditions have been carried out in triplicates, and mean values of \( K_x \) are presented in Table I.

The integration of equation (5) for boundary conditions:

\[ c_x = c^0_g \text{ for } t = 0 \text{ and } c_x = c^t_g \text{ for } t = t \text{ results in the kinetic equation of the process:} \]

\[ c_x = \exp \left( \frac{-K_x A t}{V_x} + \ln c^0_g \right) \]  
(7)

The in-time gas concentration measurements were fitted with the presented equation to obtain the \( K_x \) value (Fig. 4). To check the reproducibility, the experiments for each set of conditions have been carried out in triplicates, and mean values of \( K_x \) are presented in Table I.

<table>
<thead>
<tr>
<th>Amine</th>
<th>( K_x ) [m/s]</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.64M MDEA</td>
<td>6.00E-05 (±6.48E-06)</td>
<td>0.951</td>
</tr>
<tr>
<td>1.64M DGA</td>
<td>6.00E-04 (±4.67E-05)</td>
<td>0.998</td>
</tr>
<tr>
<td>1.64M DEA</td>
<td>1.60E-04 (±5.02E-05)</td>
<td>0.972</td>
</tr>
<tr>
<td>1.64M MEA</td>
<td>1.20E-03 (±6.83E-05)</td>
<td>0.983</td>
</tr>
<tr>
<td>1.64M MDEA+0.1P</td>
<td>4.50E-04 (±8.65E-05)</td>
<td>0.998</td>
</tr>
<tr>
<td>1.64M DEA+0.1P</td>
<td>4.50E-04 (±4.05E-05)</td>
<td>0.948</td>
</tr>
<tr>
<td>1.64M DGA+0.1P</td>
<td>1.40E-03 (±3.62E-04)</td>
<td>0.966</td>
</tr>
<tr>
<td>1.64M MEA+0.1P</td>
<td>1.50E-03 (±8.53E-05)</td>
<td>0.998</td>
</tr>
<tr>
<td>1.64M MDEA+0.5P</td>
<td>8.00E-04 (±9.27E-05)</td>
<td>0.987</td>
</tr>
<tr>
<td>1.64M DEA+0.5P</td>
<td>1.20E-03 (±3.08E-04)</td>
<td>0.977</td>
</tr>
<tr>
<td>1.64M DGA+0.5P</td>
<td>1.40E-03 (±4.66E-04)</td>
<td>0.979</td>
</tr>
<tr>
<td>1.64M MEA+0.5P</td>
<td>1.70E-03 (±1.67E-04)</td>
<td>0.997</td>
</tr>
</tbody>
</table>

Assuming the dry mode of the process, the mass transfer
resistance in the membrane is the same for each experiment performed. The influence of reactive additives ("enhancement factor") can be compared for the same relatively high liquid velocity.

By adding piperazine as an activator to amine solutions, the mass transfer coefficients increase vastly. This also has a favorable impact on the effectiveness of capturing CO\(_2\) from a gas stream. Particularly in the case of DGA and tertiary amine solutions (MDEA), activator addition helps to achieve much higher values of mass transfer coefficients compared to not activated solutions of this amines. In Table 1 are presented the results of the mass transfer coefficients for 1.64 M solutions of amines and amines with the addition of piperazine as an activator at a concentration of 0.1 M and 0.5 M. A significant improvement in carbon dioxide absorption kinetics after addition of activator for each of amines solutions can be observed, but in the case of 1.64 M MDEA + 0.5 P solution the mass transfer coefficient increased by over 90% as compared to a solution of 1.64 M MDEA, and it was the highest increase.

To determine mass transfer coefficient \(K_g\) nonlinear regression method was used. Fig. 4, presents the change of the concentration profile of carbon dioxide in time as well as the function curve estimated on the basis of the mathematical model (7). Experimental data and curve obtained by the model overlap almost perfectly.

![Graph](image1)

![Graph](image2)

Fig. 4. Kinetics of CO\(_2\) absorption in the membrane contactor for secondary (A) and tertiary (B) amines with and without presence of piperazine

Tertiary amines may be an alternative for the primary and secondary amines. Unlike the primary amines [12, 13], they do not degenerate in the presence of CS\(_2\), O\(_3\), NO\(_x\), and SO\(_x\). They are also less corrosive and require less heat during the regeneration process. MDEA has two ethanol groups and the methyl group bounded with a nitrogen atom. The absence of a hydrogen atom on the nitrogen atom causes that tertiary amines do not react directly with CO\(_2\) to form carbamates. In aqueous solutions, tertiary amines catalyze the hydrolysis reaction of the carbon dioxide forming bicarbonate ions and the protonated amine. The chemical reaction rate of MDEA and CO\(_2\) is lower than that of primary or secondary amines, however, the reaction heat released during the creation of bicarbonate is lower than that of formation carbamate, and this significantly reduces the costs associated with the regeneration of the tertiary amines [14].

The use of mixed absorbents for CO\(_2\) removal is of increasing interest. It has been found that the addition of small quantity of an activator to aqueous solutions of amines can significantly enhance the mass transfer coefficient and enhancement factor. Piperazine can be an effective activator for capturing CO\(_2\) in membrane gas absorption to improve the performance of absorbents. Piperazine has a specific molecular structure. It is a heterocyclic organic compound with symmetrical diamino-cyclic structure. Piperazine in an aqueous solution with an amine is a mild base and because of it piperazine catalyzes proton extraction in the reaction mechanism of an amine with CO\(_2\) as a result of which the chemical reaction equilibrium moves to the right, which substantially improves reaction kinetics. Piperazine can also react with CO\(_2\) as a secondary amine; this is a rapid pseudo-first-order reaction in parallel with the reaction of main amine with CO\(_2\) [15].

The results demonstrate the utilization of the tertiary amine with a low concentration of the activator (piperazine), which effectively increases the reaction kinetics. The application of the membrane contactor makes possible to carry out purification of air with carbon dioxide on a small scale by the device compact and is easy to use.

C. Long-Term Stability of the Membrane

30 mm long pieces of the membrane were immersed into the various absorbive liquids for a period of 150 days. Contact angle measurements were carried out during a long-term immersion in a selected liquid to get information about pore wetting. An example of the drop of liquid on the membrane fibers is shown in Fig. 5. The results indicated that the long term immersion of a polypropylene capillary in amine solutions has no significant effect on the wettability of the membrane. A decline in the value of the contact angle of about 10 degrees would give information about the reduction wetting angle. The difference between the values of contact angles for different liquids is associated with the contact angle measurement error, however, is not more than 5%.

![Images](image3)

Fig. 5. Droplets of 1, 64 DEA+0.1M P, day 5 (A) and 150 (B)

IV. Conclusions

Experiments have been conducted to investigate the
effectiveness of $\text{CO}_2$ removal in a membrane contactor. A single and composite (+PZ) aqueous solution of amines as absorbents was used in this study. The composite solution can maintain a higher effectiveness of $\text{CO}_2$ removal as compared with the single solution. The overall mass transfer coefficient $K_w$ with the activated solutions is much higher than that with the single solution. In the case of 1.64 M MDEA + 0.5 P solution the mass transfer coefficient increased by over 90% as compared to a not activated solution, and it was the highest growth. DGA amine solution achieved very good results in both, the reaction kinetics of the carbon dioxide and the absorption degree. These results were especially high, after piperazine had been added to DGA solution. Therefore, DGA and tertiary amines, like MDEA, can become an alternative for the primary and secondary amines. The results indicated that the long term immersion of the polypropylene capillary in amine solutions has no significant effect on the wettability of the membrane.

**NOMENCLATURE**

- $A$: gas-liquid contact area, [m$^2$]
- $c_e$: liquid phase concentration, [kg/m$^3$]
- $c_g$: gas phase concentration, [kg/m$^3$]
- $E$: enhancement factor due to chemical reaction
- $H$: Henry’s law constant, [m‘kPa/kmol]
- $K_e$: overall mass transfer coefficient, [m/s]
- $k_{e,g}$: individual gas phase mass transfer coefficient, [m/s]
- $k_{e,l}$: individual membrane mass transfer coefficient, [m/s]
- $t$: time, [s]
- $w_e$: gas velocity [m/s]
- $V_g$: volume of gas phase, [m$^3$]
- $z$: axial distance, [m]

**REFERENCES**


Anna Witek-Krowiak is an Associate Professor of the Division of Chemical Engineering in Dept. of Chemistry at Wroclaw University of Technology. She received her M.Sc. in biotechnology in 2002, PhD in chemical engineering in 2006 in Dept. of Chemistry at Wroclaw University of Technology. Her research interests focus on the diffusive and pressure driven membrane processes and sorption processes.

Anna Dawiec is a Researcher of the Division of Chemical Engineering in Dept. of Chemistry at Wroclaw University of Technology. Currently, she does her research in membrane separations as a Ph.D. candidate. She received her M.Sc. in biotechnology in 2011 in Dept. of Chemistry at Wroclaw University of Technology. Her research interests focus on the diffusive membrane processes.

Szymon Modelski is an Assistant Professor of the Division of Chemical Engineering in Dept. of Chemistry at Wroclaw University of Technology. He received his PhD (2012) in chemical engineering in Dept. of Chemistry at Wroclaw University of Technology. His research interests focus on the diffusive and pressure driven membrane processes regarding modeling and numerical simulations.

Daria Podstawczyk is a Researcher of the Division of Chemical Engineering in Dept. of Chemistry at Wroclaw University of Technology. Currently, she does her research in sorption processes as a Ph.D. candidate. She received her M.Sc. in biotechnology in 2012 in Dept. of Chemistry at Wroclaw University of Technology. Her research interests focus on the membrane and sorption processes.