

Modeling and Simulation of CO₂ Absorption in Film Membranes for Laminar Flow Conditions

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Abstract: Simulation of gas absorption in a film membrane contactor was investigated in this study. Numerical simulation was performed using computational fluid dynamics (CFD) of mass transfer in a film membrane contactor for laminar flow conditions. Physical absorption was considered in the simulations for absorption of CO₂ in pure water. Simulation results were validated with the experimental data obtained from literature for physical absorption of CO₂ in pure water. Simulation results were in good agreement with the experimental data for different values of liquid flow rate. The modeling predictions indicated that the removal of CO₂ increased with increasing liquid velocity in the membrane contactor. Also increasing temperature and gas velocity in the film membrane have an opposite effect. CFD also represents a design and optimization tool for membrane gas absorption processes.

Key words: Film membrane • Simulation • Gas absorption • Modeling • Mass transfer

INTRODUCTION

Expansion of industrial activities has caused the concentration of greenhouse gases to rise significantly in the atmosphere. This has contributed to global warming, which in turn has resulted in serious environmental problems [1]. Carbon dioxide is representing about 80% of greenhouse gases. It is reported that half of the CO₂ emissions are produced by industry and power plants using fossil fuels [2]. From the global environmental perspective, it is important to remove CO₂ to avert the threat of global warming, thereby attaining the carbon emission reduction targets set out by the Kyoto Agreement. Additionally, the CO₂ concentrations are typically 3-5% in gas-fired power plants and 13-15% in coal plants [3].

Current carbon dioxide removal technologies are based on a variety of physical and chemical processes including, absorption, adsorption, cryogenic and membrane techniques [4]. Conventional processes for the removal of CO₂ suffer from many problems such as flooding, foaming, entraining, channeling and high capital and operating costs. Therefore, many researchers have examined the possibilities of enhancing the efficiency of these processes to reduce the effect of their problems. Gas-liquid membrane contactors are expected to overcome the disadvantages of the

conventional equipment when incorporated into the gas treating processes [4]. The characteristic of gas-liquid membrane contactors is that the gas stream flows on one side and the absorbent liquid flows on the other side of the membrane without phase dispersion, thus avoiding the problems often encountered in the conventional equipment such as flooding, foaming, channeling and entrainment. For the non-wetted mode, the film membrane pores are filled with gas phase because the film membrane is hydrophobic and the pressure difference of gas-liquid is not exceeded the critical pressure. Many researchers indicated that the non-wetted mode is better than wetted mode because mass transfer in non-wetted mode is much higher than wetted mode [4].

Some experiments and theories about the gas-liquid membrane contactors had been done since Zhang and Cussler first studied the work [5]. Using polypropylene membrane, Kreulen *et al.* [6] studied absorption of CO₂ into water/glycerol mixtures. The authors studied the membrane as gas-liquid contactors in the case of both physical and chemical absorption. Separation of CO₂ from offshore gas using membrane contactors was investigated by Falk-Pederson and Dannstrom [7], who optimized the process with respect to sizes, weight and costs. Many researchers have reported the use of gas-liquid membrane contactors for absorption of CO₂ in a hydroxide solution [8], the CO₂ removal in membrane

using amino acid salts [9]. Qi and Cussler [5] studied development of a theory of the operation of gas-liquid membrane contactors and calculated mass transfer coefficients in liquid phase. They also obtained the overall mass transfer coefficients, including resistances in both liquid and membrane and compared the performance of membrane contactors with that of packed towers.

Karoor and Sirkar [10] investigated the separation of CO_2 and SO_2 from CO_2/N_2 and SO_2/air gas mixtures, using water as an absorbent in a parallel module employing microporous polypropylene membrane. A similar system has been recently studied by Zhang *et al.* [11] for co-current gas-liquid contact. In both studies, the authors assumed negligible axial diffusion, which may not be a good assumption, especially for low gas velocities. Kim and Yang [12] investigated the separation of CO_2/N_2 mixtures using membrane contactors theoretically and experimentally. Although there was an agreement between the model predictions with experimental results, the authors assumed a linear decrease of gas flow rate for the simulation purposes.

Thus, there is a definite need for a mass transfer model that can provide a general simulation of the chemical and physical absorption in gas-liquid membrane contactors. The main purpose of this study is to solve a 2D mathematical model for absorption of CO_2 in film membrane contactors. The model is then validated using experimental data obtained from literature for absorption of CO_2 in water. Influence of different process parameters will be investigated on the mass transfer and absorption of CO_2 in membrane contactor.

Theory: A comprehensive two-dimensional mathematical model was used for the transport of carbon dioxide through film membrane contactors. In this work we study the absorption of pure CO_2 and absorption of CO_2 from CO_2/N_2 gas mixture in pure water as absorbent in a film membrane contactor. The model was based on “non-wetted mode” in which the gas phase filled the membrane pores for co-current gas-liquid contacts. Laminar velocity distributions were used for the gas and liquid flow in the membrane contactor.

Model Equations: A 2D mass transfer model was used for a film membrane, as shown in Fig. 1. The gas flows with a fully developed laminar velocity in the one side and the liquid absorbent (pure water) flows with laminar flow in the other side. Fig. 1 shows the cross sectional area of the film membrane contactor. The steady state two-dimensional mass balances are carried out for membrane contactor. The gas phase is fed to the one side (at $z = 0$), while the absorbent is passed through the other side (at $z = 0$). CO_2 is removed from the gas mixture by diffusing through the membrane and then is absorbed in the solvent (water).

The model is built considering the following assumptions:

- Steady state and isothermal conditions.
- Fully developed gas and liquid velocity profile in the film membrane.
- Ideal gas behavior is imposed.
- The Henry's law is applicable for gas-liquid interface.
- Laminar flow for gas and liquid flow in the contactor.
- Non-wetted mode in which the gas filled the membrane pores.

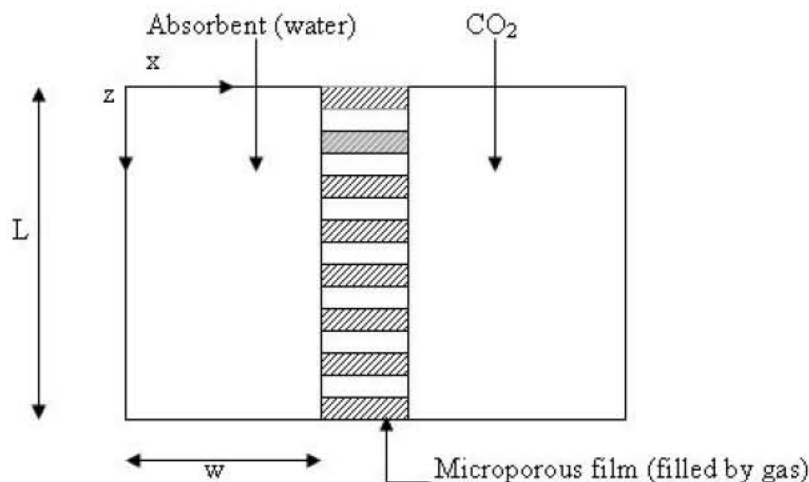


Fig. 1: Schematic drawing of CO_2 absorption in film membrane.

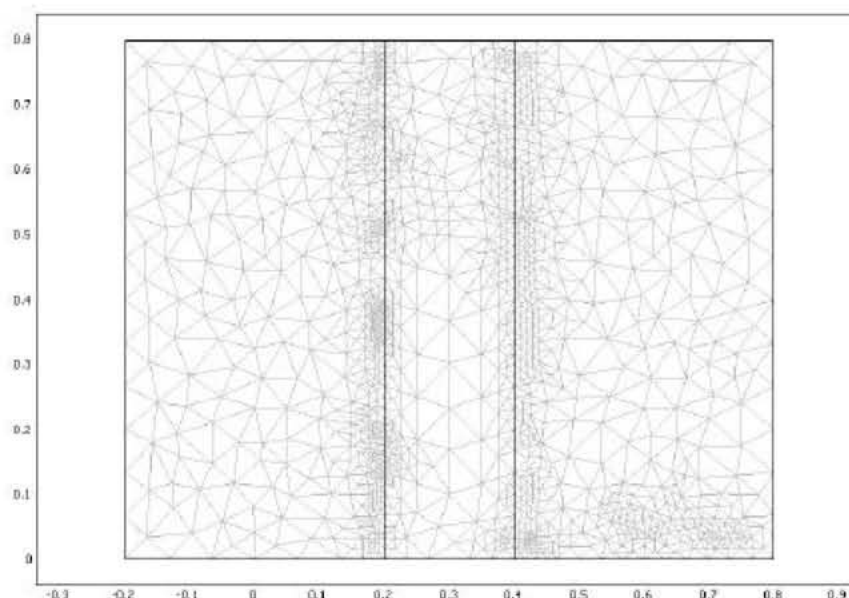


Fig. 2: Magnified segment of the mesh used in the numerical simulation. There are 1025 elements in total for the whole domain. z -Direction scale factor = 100. The three domains from left to right are liquid phase, film membrane and gas phase, respectively.

The continuity equation for each species in a reactive absorption system can be expressed as [13]:

$$\frac{\partial C_i}{\partial t} = -(\nabla \cdot C_i V) - (\nabla \cdot J_i) + R_i \quad (1)$$

Where C_i , J_i , R_i , V and t are the concentration, diffusive flux, reaction rate of species i , velocity and time, respectively. Either Fick's law of diffusion or Maxwell–Stefan theory can be used for the determination of diffusive fluxes of species i .

The continuity equation for steady state for CO_2 in the three sections of film membrane contactor is obtained using Fick's law of diffusion for estimation of diffusive flux:

$$D_{\text{CO}_2} \left[\frac{\partial^2 C_{\text{CO}_2}}{\partial x^2} + \frac{\partial^2 C_{\text{CO}_2}}{\partial z^2} \right] = V_z \frac{\partial C_{\text{CO}_2}}{\partial z} \quad (2)$$

In a laminar flow, a fully developed velocity profile can be described as [13]:

$$V_z = 6\bar{V} \left[\left(\frac{x}{w} \right) - \left(\frac{x}{w} \right)^2 \right] \quad (3)$$

Where \bar{V} is the average velocity in the film membrane. The boundary conditions for mass transfer equations are:

$$\text{at } z=0, C_{\text{CO}_2} = C_0 \quad (4)$$

$$\text{at } x=0, \frac{\partial C_{\text{CO}_2}}{\partial x} = 0 \quad (5)$$

$$\text{at } x=w, C_{\text{CO}_2} = C_{\text{CO}_2, \text{gas}} \times m \quad (6)$$

Where m is the physical solubility of CO_2 in the liquid absorbent (pure water).

Method of Numerical Solution: The dimensionless model equations with the appropriate boundary conditions were solved using COMSOL software, which uses finite element method (FEM) for numerical solutions of differential equations. The finite element analysis is combined with adaptive meshing and error control using numerical solver of UMFPACK. This solver is an implicit time-stepping scheme, which is well suited for solving stiff and non-stiff non-linear boundary condition. We used an IBM-PC-Pentium4 (CPU speed was 2800 MHz) to solve the set of equations.

Fig. 2: Shows a segment of the mesh used to determine the gas transport behavior in film membrane contactor. It should be pointed out that the COMSOL mesh generator creates tetrahedral that are isotropic. A scaling factor of 100 has been employed in z -direction due to large difference between x and z . COMSOL automatically scales back the geometry after meshing. This generates an anisotropic mesh around 1025 elements.

RESULTS AND DISCUSSION

The calculations are performed for the cases of pure CO₂ and CO₂/N₂ mixture. The CO₂ inlet concentration in case of CO₂/N₂ mixture is taken as 20 vol.%. The gas phase concentration was assumed constant in the simulations. The length of the film membrane considered in this study, is 0.8m and the distance between the contactor wall and the membrane is 0.02 m. A liquid velocity of 0.1 m s⁻¹ is used in the simulations.

The solubility of CO₂ in pure water and the diffusion coefficient of CO₂ in the water and N₂ were taken from the Appendix [14, 15].

Model Validation: In order to validate the mass transfer model and the numerical solution, our modeling predictions for the physical absorption of 20% CO₂ in pure water using film membrane contactor is compared with the experimental values reported by Wang *et al.* [16] (Fig. 3). The membrane geometry and operating parameters used in the simulation are the same as those used by Wang *et al.* [16]. As shown in Fig. 3, the simulation results are in good agreement with the literature data of Wang *et al.* [16] for different values of liquid flow rates, the average deviation being about 7%. It is worth mentioning here that while studying the effect of liquid velocity or liquid flow rate on the CO₂ absorption flux in water for different liquid flow rates, it was found that much lower values of liquid velocity has distinct influence on the CO₂ absorption flux.

Effect of Liquid Flow Rate on the Absorption of CO₂:

The percentage removal of CO₂ can be calculated from the equation below:

$$\% \text{ removal CO}_2 = 100$$

$$\frac{(v \times C)_{inlet} - (v \times C)_{outlet}}{(v \times C)_{inlet}} = 100 \left(1 - \frac{C_{outlet}}{C_{inlet}} \right) \quad (7)$$

Where v and C are the volumetric flow rate of gas phase and concentration, respectively. C_{outlet} is calculated by integrating the local concentration at outlet of membrane ($z = L$):

$$C_{outlet} = \frac{\iint_{z=L} C(x) dA}{\iint_{z=L} dA} \quad (8)$$

The change in volumetric flow rate is assumed to be negligible and thus % CO₂ removal can be approximated by Eq. (7).

In Fig. 4, the CO₂ outlet concentration in the gas phase is plotted as a function of absorbent flow rate or velocity and Fig. 5 illustrates the variation of the percentage removal of CO₂ as a function of liquid flow rate or velocity. As the absorbent flow rate increases, the mass transfer rate of carbon dioxide into the liquid increases because the concentration gradients of CO₂ and absorbent in the liquid increase, thus the CO₂ outlet concentration in gas decreases (Fig. 4) and the percentage removal of CO₂ increases (Fig. 5). The figures clearly indicate that liquid flow rate in the film membrane contactor has significant effect on the removal of CO₂.

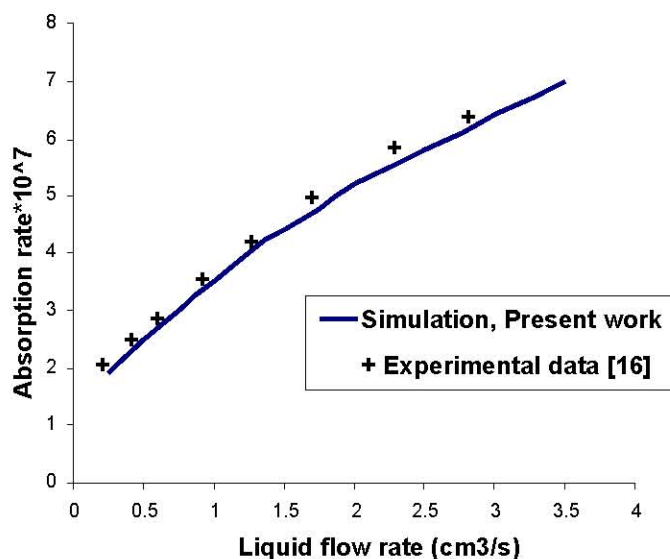


Fig. 3: Comparison of the CO₂ absorption rate in water with the experimental data [16].

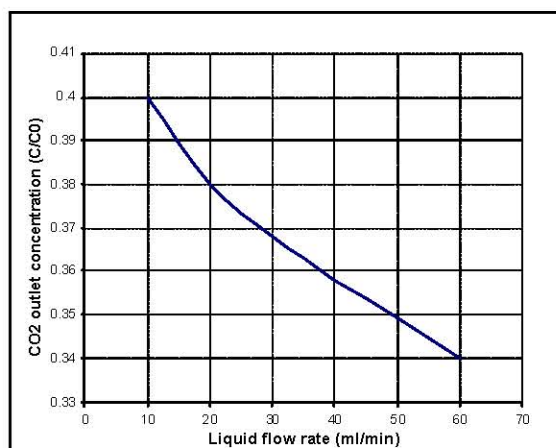


Fig. 4: Relationship between CO₂ outlet concentration in the gas phase and liquid flow rate . Gas pressure= 121.3 kPa, temperature= 298 K, Gas flow rate=100 ml/min. Inlet gas phase is 20% CO₂ & 80% N₂.

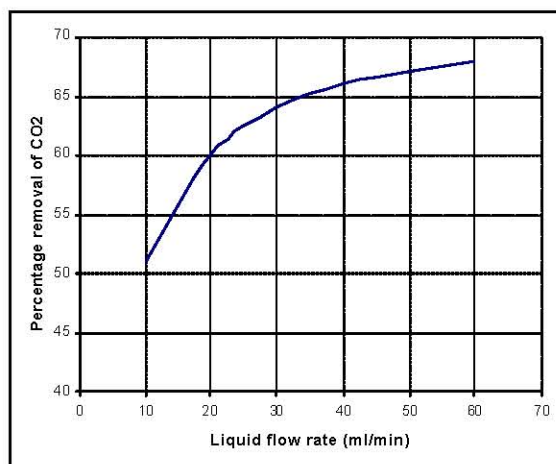


Fig. 5: Relationship between percentage removal of CO₂ and liquid flow rate. Gas pressure= 121.3 kPa, temperature= 298 K, Gas flow rate= 300 ml/min. Inlet gas phase is 20% CO₂ & 80% N₂.

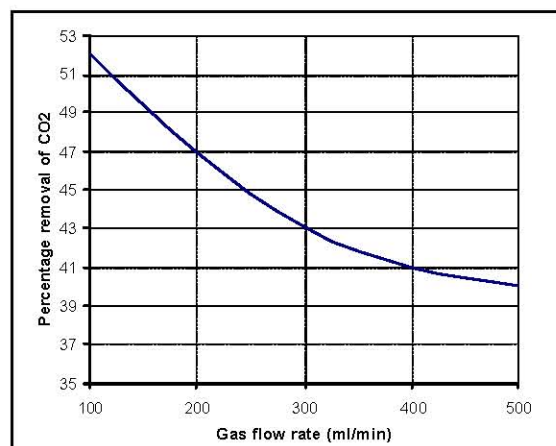


Fig. 6: Effect of gas phase flow rate on the removal of CO₂. Gas pressure = 121.3 kPa, liquid flow rate= 100 ml/min. Inlet gas phase is 20% CO₂ & 80% N₂.

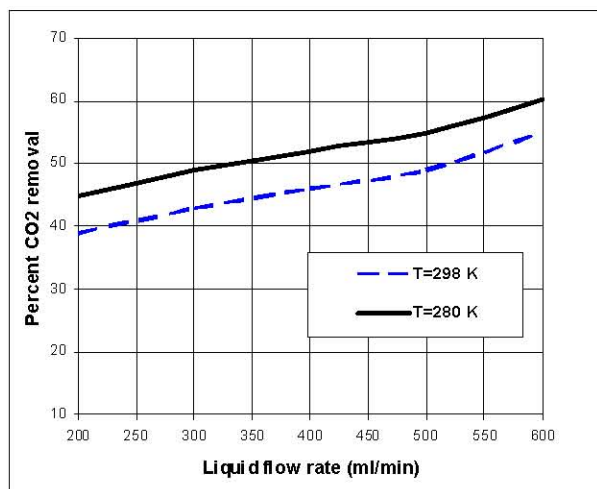


Fig. 7: Effect of temperature on the CO₂ removal in the gas phase. Gas pressure= 121.3 kPa, Gas flow rate= 500 ml/min. Inlet gas phase is 20% CO₂ & 80% N₂.

Effect of Gas Flow Rate on the Removal of CO₂: The percentage removal of CO₂ in the gas phase along the length of film membrane contactor for different values of gas flow rates (the effect of convection term) is presented in Fig. 6. As expected, the increase in the gas flow rate reduces the residence time in the membrane contactor, which in turn reduces the removal rate of CO₂ in the contactor. The percentage removal of CO₂ decreases from 52% to 40% when the gas flow rate in the film membrane contactor changes from 100 ml/min to 500 ml/min. Also the Fig. 6 indicates that gas flow rate dose not greatly affect the CO₂ removal in the membrane contactor.

Effect of Temperature: The change in temperature affects the key process parameters such as solubility of CO₂ in water, diffusion coefficients of gas and liquid phase and gas flow rate. Therefore, temperature variations are expected to results in significant changes in the mass transfer of CO₂. Fig. 7 shows the effect of temperature on the CO₂ removal. It is seen from figure that with decreasing temperature, the CO₂ removal increases. This can be attributed to the fact that as the temperature decreases, the physical solubility of CO₂ in water increases and the volumetric gas flow rate decreases, which gives combined favorable effects on the CO₂ removal. On the other hand, with decreasing temperature, liquid-phase diffusion coefficients decrease, giving unfavorable effect on the CO₂ removal. Since the favorable effect is more pronounced than the unfavorable effect, a net enhancement of CO₂ removal is observed with decreasing temperature.

CONCLUSION

This work presents a numerical simulation of mass transfer in a film membrane contactor for gas–liquid phase process. The numerical simulation was based on solving the conservation equations for gas in the membrane contactor. The influence of various process parameters on the mass transfer of CO₂ was investigated. The simulation results were compared with the experimental data obtained from literature for absorption of CO₂ in pure water. The simulation results were in good agreement with the experimental data for different values of liquid flow rate. The results for the physical absorption of CO₂ in water indicated that the removal of CO₂ increased with increasing liquid velocity in the film membrane contactor. On the other hand, increasing temperature and gas velocity in the membrane seemed to have an opposite effect. The liquid flow rate in the film membrane contactor has significant effect on the removal of CO₂ whereas, the gas flow rate dose not greatly affect the CO₂ removal in the membrane.

Nomenclature

A	cross section of membrane (m ²)
C_0	inlet gas concentration (mol/m ³)
C	concentration (mol/m ³)
C_{CO_2}	CO ₂ concentration in the membrane (mol/m ³)
D	Diffusion coefficient (m ² /s)
D_{CO_2}	Diffusion coefficient of CO ₂ (m ² /s)
D_{w,CO_2}	Diffusivity of CO ₂ in pure water (m ² /s)

$D_{CO_2-N_2}$	Diffusion coefficient of CO ₂ in N ₂ (m ² /s)
J	Diffusive flux (mol/m ² s)
L	Length of the film (m)
m	Physical solubility (dimensionless)
m_{w,CO_2}	Distribution coefficient of CO ₂ in pure water (dimensionless)
P	Pressure (Pa)
T	Temperature (K)
\bar{V}	Average velocity in the membrane (m/s)
V_z	Z-velocity in the contactor (m/s)
W	Width between wall and membrane (m)
X	Distance (m)
Z	Distance (m)

Greek symbols

v volumetric flow rate (m³/s)

Subscripts

i	species i
g	Gas
in	Inlet
out	Outlet
l	liquid

Appendix

A.1. Solubility: The distribution coefficient of CO₂ in pure water was taken from Versteeg and van Swaaij [14]:

$$m_{w,CO_2} = 3.59 \times 10^{-7} RT \exp\left(\frac{2044}{T}\right) \quad (\text{dimensionless}) \quad (A.1)$$

A.2. Diffusivity: The diffusivity of CO₂ in pure water, D_{w,CO_2} was taken from Versteeg and van Swaaij [14]:

$$D_{w,CO_2} = 2.35 \times 10^{-6} \exp\left(\frac{-2119}{T}\right) \quad \text{m}^2/\text{s} \quad (A.2)$$

The diffusivity of CO₂ in N₂ can be calculated based on Chapman–Enskog theory [15]:

$$D_{CO_2-N_2} = 1.21 \times 10^{-5} \text{ m}^2/\text{s} \quad (A.3)$$

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