

Simulation of Gas/Liquid Membrane Contactor via COMSOL Multiphysics ®

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Abstract: A comprehensive mathematical model that includes mass, momentum and heat transfer was developed for the transport of gas mixture of carbon dioxide and methane through hollow fiber membrane contactors. COMSOL was used in solving the set of partial, ordinary and algebraic equations. The model was based on "non-wetted mode" in which the gas mixture filled the membrane pores for countercurrent gas-liquid contact. Axial and radial diffusion inside the hollow fiber membrane, through the membrane skin, and within the shell side of the contactor were considered in the model. Furthermore, the model was validated with the experimental results obtained for carbon dioxide removal from CO₂/CH₄ gas mixture using custom made polyvinylidene fluoride (PVDF) membrane contactor. The effect of inlet gas and liquid temperature on the membrane performance was investigated. The effect of module packing factor was also investigated. The modeling predictions were in good agreement with the experimental results.

Keywords: COMSOL, modeling, simulation, membrane contactor, CO₂ absorption.

1. Introduction

Several techniques are available for the separation of CO₂ from flue gas streams at present, such as chemical and physical absorption, solid adsorption, carbon molecular sieve adsorption, cryogenic distillation, membrane separation [1] and other novel methods [2]. Among these methods, the most well established method is to separate CO₂ from gas stream by absorption into alkanolamines solutions using conventional contactor equipment such as packed or tray columns [3]. In packed towers or columns, CO₂ contacts the absorbent to form a weak complex and the aqueous solution is then transferred to a regenerating unit to release CO₂ by heating. After this, the solution is cooled and re-

circulated to the absorption equipment. Although chemical absorption technology has large commercial significance, the technology is energy-consuming and not easy to operate because of some frequent problems including foaming, flooding, channeling and entrainment. should be organized to best present the material.

Membrane gas absorption technology uses hollow fiber membrane contactors to absorb CO₂ from flue gas into solvent. By contrast, chemical absorption technology uses random or structured packed columns to capture CO₂ from flue gas into solvent. Hydrophobic microporous membranes are used to form a permeable barrier between the liquid and gas phases; Absorbent liquid offers the CO₂ selectivity; liquid phase and gas phase are not directly contacted; main driving force is the differential concentration of CO₂ between gas phase and liquid phase; membrane pores must be completely filled by gas.

Liquid phase and gas phase are not directly contacted. Avoid the conventional problems such as flooding, foaming, channeling and entrainment in packed column. Membrane device has larger contact area. Reduction over 70% in size and 66% in weight compared with conventional columns. The interfacial area is known and constant. It does not depend on the operating conditions such as temperature and liquid flow rate. As a result, it is easier to predict the performance of a membrane contactor [4].

Potential problems of membrane gas absorption are membrane wetting. Main difficulty is how to prevent the membrane wetting in the long-term operations. This can be achieved by using hydrophobic membranes through surface modification of membrane, composite membrane, selection of denser hollow fiber membrane; selection of liquid with suitable surface tension and optimizing the operating conditions.

An amino acid salt potassium glycinate was found to have high tension, high reactivity with

CO₂, and chemical compatibility with membrane material and easiness of regeneration [5].

2. Use of COMSOL Multiphysics

A steady state mathematical model that described the material balance has been carried out on a shell-and-tube membrane contactor system (Figure 1)

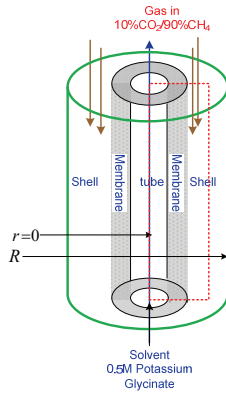


Figure 1. Schematic diagram of the hollow fiber section used in modeling the membrane contactor

The model is developed for a segment of a hollow fiber, as shown in Fig. 4, through which the solvent flows with a fully developed laminar parabolic velocity profile. The fiber is surrounded by a laminar gas flow in an opposite direction to that of the liquid. Based on Happel's free surface model [37], only portion of the fluid surrounding the fiber is considered which may be approximated as circular cross section. Thus, symmetry may be considered at the outer portion of the fluid surrounding the fiber (at $r = r_3$). The steady state continuity equation for each species during the simultaneous mass transfer and chemical reaction in a reactive absorption system can be expressed as:

2.1 Shell side (gas phase)

The steady state material balance for the transport of gas mixture in the shell side may be written as follows ($i = \text{CO}_2$ and CH_4):

$$D_{i,s} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_{i,s}}{\partial r} \right) + \frac{\partial^2 C_{i,s}}{\partial z^2} \right] = \frac{\partial}{\partial z} (V_{zs} C_{i,s}) + \frac{1}{r} \frac{\partial}{\partial r} (r v_{rs} C_{i,s})$$

Considering the active area around each fiber calculated from the hypothetical radius bearing in

mind a hexagonal-shaped unit cell of the fiber assembly around each fiber.

$r_3 = r_2 \sqrt{1 / (1 - \phi)}$ where ϕ is the volume void fraction of the membrane contactor module. Assuming Happel's free surface model, the boundary conditions:

$$r = r_2, C_{i,s} = C_{i,m}$$

$$r = r_3, -\frac{\partial C_{i,s}}{\partial r} = 0$$

$$z = 0, -\frac{\partial C_{i,s}}{\partial r} = 0$$

$$z = L, C_{\text{CO}_2,s} = C_{\text{CO}_2}^o, C_{\text{CH}_4,s} = C_{\text{CH}_4}^o$$

2.2 Membrane section

The steady state material balance for the transport of CO₂ and CH₄ across the membrane skin layer for non-wetting mode of operation is considered to be due to diffusion only; no reactions are taking place in the gas filled pores ($i = \text{CO}_2$ and CH₄).

$$D_{i,m} \left[\frac{\partial^2 C_{i,m}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{i,m}}{\partial r} + \frac{\partial^2 C_{i,m}}{\partial z^2} \right] = 0$$

Boundary conditions:

$$r = r_1, C_{i,m} = C_{i,t} / m_i$$

$$r = r_2, C_{i,m} = C_{i,s}$$

$$z = 0, z = L, \frac{\partial C_{i,m}}{\partial z} = 0$$

where m_i is the solubility of CO₂ and CH₄ in aqueous sodium hydroxide solution.

2.1 Tube Side (liquid phase)

The steady state material balance for the transport of CO₂ and aqueous PG in the lumen side of the hollow fiber membrane tubes is considered to be due to diffusion, convection and reaction as well:

$$D_{i,t} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_{i,t}}{\partial r} \right) + \frac{\partial^2 C_{i,t}}{\partial z^2} \right] + r_{i,t} = \frac{\partial}{\partial z} (v_{zt} C_{i,t}) + \frac{1}{r} \frac{\partial}{\partial r} (r v_{rt} C_{i,t})$$

where the subscript "i" indicates carbon dioxide and sodium hydroxide. Reaction rates for CO₂

and PG are shown in equations 13 and 14, respectively:

$$r_{CO_2,t} = -k_r C_{CO_2,t} C_{PG}$$

$$r_{PG} = -k_r C_{CO_2,t} C_{PG}$$

Boundary conditions:

The boundary conditions for liquid flowing in lumen side of the fibers ($i = CO_2$ and PG):

$$r = 0, \quad -\frac{\partial C_{i,t}}{\partial r} = 0$$

$$r = r_1, \quad C_{i,t} = m_i C_{i,m}$$

$$z = 0, \quad C_{NaOH,t} = C_{NaOH}^0$$

$$z = L, \quad -\frac{\partial C_{i,t}}{\partial z} = 0$$

2.3 Energy balance

Shell side

The steady state energy balance equations for shell side, membrane section and tube side are developed as follows (No reaction is taking place in the shell gas side):

$$\rho_g C_{pg} \left(v_{rs} \frac{\partial T_s}{\partial r} + v_{zs} \frac{\partial T_s}{\partial z} \right) = k_g \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_s}{\partial r} \right) + \frac{\partial^2 T_s}{\partial z^2} \right]$$

Boundary conditions:

$$r = r_2, \quad T_s = T_m,$$

$$r = r_3, \quad \frac{\partial T_s}{\partial r} = 0,$$

$$z = 0, \quad \frac{\partial T_s}{\partial z} = 0$$

$$z = L, \quad T_s = T_{0,g}$$

Membrane section

Accordingly, the steady state thermal energy equation for the gas and membrane that are at the thermal equilibrium conditions, is simplified to

$$0 = \left[k_m \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_m}{\partial r} \right) + k_m \frac{\partial^2 T_m}{\partial z^2} \right]$$

Boundary conditions:

Assuming the heat of evaporation is taking place at liquid-membrane interface.

$$r = r_1, \quad -k_t \frac{\partial T_t}{\partial r} = -k_m \frac{\partial T_m}{\partial r} + J_w \Delta H_{evap}$$

$$r = r_2, \quad T_m = T_s,$$

$$z = 0, \quad z = L, \quad -\frac{\partial T_s}{\partial z} = 0$$

Here, J_w is the water evaporation flux (mol/m² s), ΔH_{evap} is the enthalpy change of evaporation (J/mol).

$$k_m = \varepsilon k_s + (1 - \varepsilon) k_g$$

where ε is the membrane porosity, k_g and k_s refer to the thermal conductivity coefficients of gas within the membrane pores and the solid membrane, respectively.

Tube side (Liquid phase):

In the tube side heat is transferred through, conduction, convection and through solvent evaporation as well.

$$\rho_L C_{pl} \left(v_{rt} \frac{\partial T_t}{\partial r} + v_{zt} \frac{\partial T_t}{\partial z} \right) = k_L \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_t}{\partial r} \right) + \frac{\partial^2 T_t}{\partial z^2} \right] + r_{CO_2} \Delta H_{rxn}$$

Boundary conditions:

$$r = 0, \quad -\frac{\partial T_t}{\partial r} = 0,$$

$$r = r_1, \quad -k_t \frac{\partial T_t}{\partial r} = -k_m \frac{\partial T_m}{\partial r} - J_w \Delta H_{evap}$$

$$z = 0, \quad T_t = T_{t,0},$$

$$z = L, \quad -\frac{\partial T_t}{\partial z} = 0$$

More details and the parameters used in the simulation can be found elsewhere [6]. The simultaneous partial differential equations were solved using software COMSOL Multiphysics.

3. Experimental

The schematic diagram of the experimental setup used in CO₂ absorption is shown in Fig. 2. In this experiment the effect of inlet absorbent temperature on system performance is investigated. Inlet and exit temperatures of the

liquid and gas streams were measured using temperature sensors located at the inlet and exit of both liquid and gas streams. The water evaporated from the absorbent liquid at various absorbent inlet temperatures is condensed and collected using refrigerated cooling water bath and condenser. The gas free water vapor is sent to the gas chromatography (GC). The gas GC is used to measure the CO₂ concentration in the exit gas stream. The amount of condensed water vapor is weighed using high precision digital balance placed under the collecting vessel.

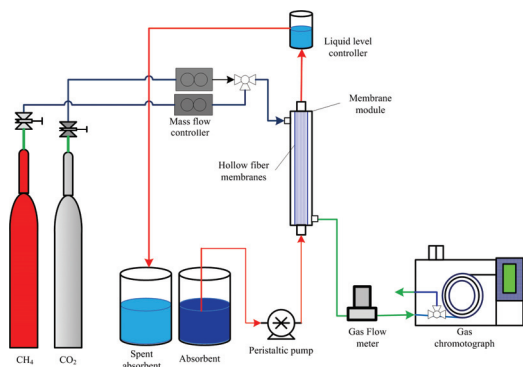


Figure 2. Schematic diagram of gas absorption unit

4. Results and Discussion

The surface diagram generated for the set of model equations generated from the mass balance around the membrane module was solved via COMSOL software package and depicted in Figure 3. The diagram depicts the CO₂ concentration across the membrane module. The diagram revealed a complete removal of carbon dioxide is achieved within the first 0.12 m of the membrane length as shown from the blue color on the shell side at a dimensionless length of 0.6, as the gas is entering counter currently with liquid solvent (0.5 M potassium glycinate), accordingly the length of the fiber is 0.6 of the 0.26 m length of fibers (0.156 m).

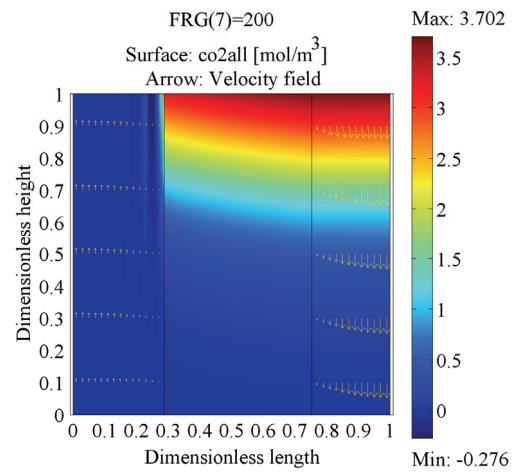


Figure 3. Surface plot for CO₂ removal via potassium glycinate in a membrane contactor

Figure 4 shows a comparison between experiment results and model prediction at various inlet solvent temperatures. The results revealed that carbon dioxide removal flux increased with increased solvent inlet temperature. That is attributed to increased rate constant with temperature, hence, increased reaction rate removal flux.

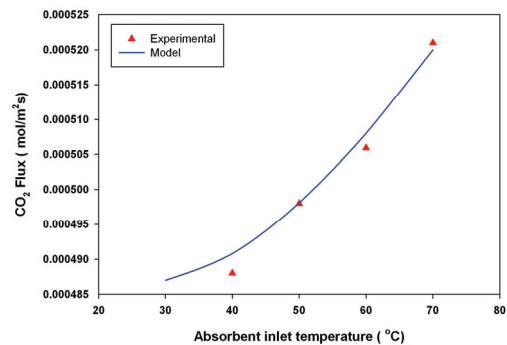


Figure 4. Effect of potassium glycinate temperature on CO₂ removal flux

5. Conclusions

PVDF hollow fiber membrane was fabricated successfully via thermally induced phase separation. The in-house fabricated membrane

was utilized as gas-liquid membrane contactor module. The constructed module was used for the removal of CO₂ from natural gas using potassium glycinate as solvent. Complete removal was achieved using potassium glycinate as solvent. The model prediction and experimental results were in good agreement with model prediction.

6. Nomenclature

A	Total area of membrane, m ²
C_i	Concentration of component i
$C_{i,m}$	Concentration of component i
$C_{i,s}$	Concentration of component i
$C_{i,t}$	Concentration of component i
D_i	Diffusion coefficient of component
d_p	Pore diameter, m
d_m	Module diameter, m
h_m	Mass transfer coefficient, m s ⁻¹
k_m	Thermal conductivity of solid
k_ε	Gas filled pores thermal conductivity
L	Length of hollow fiber membrane, m
m	Physical solubility
M	Molecular weight of gas, g mol ⁻¹
p	Pressure, Pa
r_1	Inner tube radius, m
r_2	Outer tube radius, m
r_3	Estimated module radius, m
R	Dimensionless radius, m
R_g	Universal gas constant,
R_{evap}	Rate of solvent evaporation
T_m	Membrane section temperature, K
T_s	Shell side temperature, K
T_t	Tube side temperature, K
v_{ot}	Solvent inlet velocity it tube side, m s ⁻¹
v_{os}	gas side inlet velocity it tube side, m s ⁻¹
v_r	Velocity of fluid inside the module
v_z	Velocity of fluid inside the
z	Axial distance, m

Greek letters

ρ	Gas density, g cm ⁻³
μ	Viscosity of gas, Pa s
ε_s	Membrane surface porosity
\mathcal{E}	Membrane bulk porosity

7. References

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