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MODELING AND SIMULATION OF CARBON DIOXIDE ABSORPTION IN MONOETHANOLAMINE IN PACKED ABSORPTION COLUMNS

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ABSTRACT. Computer-based process simulations are today recognized as an essential tool to be applied in chemical process industries. For this paper a mathematical model is needed to describe closer the real physical – chemical processes that take place in a reactor (packed absorption column) used for carbon dioxide absorption in mono-ethanolamine aqueous solution.

The mathematical model was developed for analyzing absorption rate and understanding of micro level interaction of various processes taking place inside de absorption column. The modeling includes transfer processes: mass and heat to study the coupled effect of temperature and concentration on the rate of absorption. The reaction kinetics and the vapor-liquid equilibrium (VLE) are other important parts of the mathematical model. The developed equations include both ordinary differential equations and partial differential equation. The discretization was used to transform partial differential equations in ordinary ones.

The evolutions (in time and space) of the processes parameters (liquid and gaseous flows, composition of the streams, temperatures etc.) were studied for carbon dioxide absorption process.

Keywords: *Chemical absorption, Packed column, Stationary-dynamic model*

INTRODUCTION

The protection of the environment is a significant problem of modern human society for a sustainable development. For environmental protection and climate change mitigation, the reports of Intergovernmental Panel on Climate Change established on scientific basis that climate change and rising of global temperature levels noticed in the past 50 years are undoubteful linked with human activity and greenhouse gas emissions (mainly carbon dioxide) [1]. At the same time with realizing the danger there had been adopted strict laws to control the emission of polluting substances. From different greenhouse gases, the most important from the volume of emissions is carbon dioxide.

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For the limitation of climate changes, the goal is to reduce the emission of carbon dioxide by capture and storage techniques. For carbon dioxide capture there are multiple technological options: capture from combusted gases resulted after the burning of fuels (post-combustion capture), capture before the burning of fuels (pre-combustion capture), or the oxy-combustion technique where the fuels are burned in oxygen, not in air, and after the condensation of the water from the burnt gases carbon dioxide can be captured and stored because it is the main component. Once carbon dioxide captured, has to be stored in safety under special conditions for a long period of time [2,3].

Nowadays the absorption of carbon dioxide in alkanolamines is the most common technology and one of the few technological options viable for large CO_2 removal process (to be applied for instance in power generation sector). Economic studies show that this method will be competitive also in the future. To extensive laboratory work, modeling and simulation of absorption process are needed in order to evaluate the process.

This paper aims to develop a dynamic mathematical model for carbon dioxide absorption in aqueous solution of mono-ethanolamine in packed absorption columns. The main purpose of the paper is to develop and than to validate a model which can be then used in various operation condition for optimization of techno indicators of carbon dioxide absorption process.

RESULTS AND DISCUSSION

Mathematical model of absorption column

Carbon dioxide absorption using alkanolamines falls in the general category of chemical gas – liquid absorption [4,5]. In Figure 1, a simplified flowsheet of a carbon dioxide capture using mono-ethanolamine (MEA) is presented. The setup consist of 3 major sections [5]: (1) reactor-absorption section (tower column called), (2) the liquid low section consisting the peristaltic pump and (3) gas collection section with the gas flow composition and pressure measurement apparatus. In absorption column with stuffing, the liquid and a gas flowing in opposite directions, enable a chemical component to be transferred from the gas phase to the liquid phase. The gas enters at the base of the absorption column, it flow rates being determined by variable area flow meters. The liquid to the top of the column is similarly metered and falls through the packing where it is contacted with the rising gas.

A mathematical model has been developed for prediction the rate absorption of carbon dioxide into aqueous solution of mono-ethanolamine (MEA). The basic assumption considered for the CO_2 absorption by mono-ethanolamine solution in an absorption column with Raschig rings are presented below:

- Model parameters are constant in the radial cross section of the column (piston-type flow);
- Both gas and solids velocities are considered constant;

- Heat transfer by conduction and radiation are negligible in the axial direction;
- Carbon dioxide solubility in liquid phase is in accordance with the Henry's law;
- Phase liquid is not volatile in the process temperature;
- Chemical reaction takes place only in the film of liquid;
- The absorption columns is operated adiabatic;
- Both phases (liquid and gas) are considered ideal mixtures.

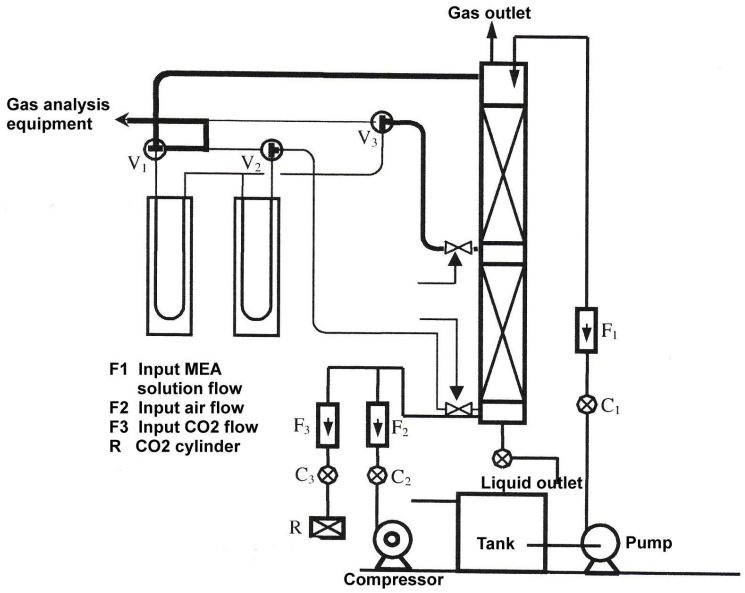

Figure 1. Gas – liquid packed absorption column

Chemical absorption of carbon dioxide can be done using base chemicals like alkaline hydroxides, ammonia or organic compounds (e.g. alkanolamine). The absorption of CO_2 into alkanolamine solution involves a chemical reaction of a weak base (alkanolamine) with a weak acid (CO_2). The chemical equilibrium takes place in the liquid phase, when carbon dioxide is absorbed in an aqueous solution of alkanolamines.

The overall chemical reaction occurring in the liquid phase between CO_2 and mono-ethanolamine (MEA) may be expresses as follow:

$$CO_2 + 2\ RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^-$$

where R indicates $HOCH_2CH_2$-. This chemical reaction is second order, respectively is first order with respect to CO_2 and MEA separately [5], and

the reaction rate (r), can be defined in function of the molar concentration of reactants, as follows: $r=k*C_A*C_B$ [5], where k is the reaction rate constant The temperature dependence of the reaction rate constant is presented bellow [3]:

$$k = 4.4 \cdot 10^8 \cdot e^{\left(\frac{5400}{T}\right)} m^3/mol \cdot s \tag{1}$$

The model equations include both partial differential equations and algebraic equations. The model contains basically mass and heat conservation equations presented below [3,6,7]. A list of abbreviations used is presented at the end of the paper.

The mass balance for liquid phase is described by the equations of consuming both reactants (mono-ethanolamine and carbon dioxide):

$$\frac{\partial C_A}{\partial t} = -v_L \cdot \frac{\partial C_A}{\partial z} - k \cdot C_A \cdot C_B + E \cdot K_G \cdot a_u \cdot \left(C_{AG} - H_{CO_2} \cdot C_A\right)$$
$$\frac{\partial C_B}{\partial t} = -v_G \cdot \frac{\partial C_B}{\partial z} - b \cdot k \cdot C_A \cdot C_B \tag{2, 3}$$

The effect of a chemical reaction is given by the enhancement factor, E, defined as the ratio of the absorption rate of a gas into a reacting liquid to that if there was no reaction [7]. The enhancement factor can be approximated [6,7]:

$$E = \sqrt{k \cdot D_{CO_2,G} \cdot C_B} \Big/ k_L \tag{4}$$

The heat balance equation for the liquid phase is presented in the following equation (the chemical reaction between carbon dioxide and mono-ethanolamine is exothermic):

$$\frac{\partial T_L}{\partial t} = -v_L \cdot \frac{\partial T_L}{\partial z} - \frac{\Delta_R H \cdot k \cdot C_A \cdot C_B}{\rho_{sol} \cdot c_{p_{sol}}} + \frac{h \cdot a_u}{\rho_{sol} \cdot c_{p_{sol}}} \cdot \left(T_G - T_L\right) \tag{5}$$

The heat transfer coefficient in the gas phase was found by using the Chilton-Colburn analogy. The value of the heat transfer coefficient depends of the gas density, diffusivity, heat capacity and thermal conductivity.

The mass balance for gas phase is described by the equation of consuming carbon dioxide:

$$\frac{\partial C_{AG}}{\partial t} = -v_G \cdot \frac{\partial C_{AG}}{\partial z} - E \cdot K_G \cdot a_u \cdot \left(C_{AG} - H_{CO_2} \cdot C_A\right) \tag{6}$$

The heat balance equation for the gas phase is presented in the following equation:

$$\frac{\partial T_G}{\partial t} = -v_G \cdot \frac{\partial T_G}{\partial z} - \frac{h \cdot a_u}{c_{p_G} \cdot \rho_G} \cdot (T_G - T_L) \tag{7}$$

Table 1. Parameters of the model

Absorption column parameters:	
Height	H = 1.4 *m*
Diameter	D = 0.075 *m*
Specific area	a_u= 440 m^2/m^3
Input flows:	
Gas flow	F_G = 2*10^{-3} m^3/s
Liquid flow	F_L = 3.42*10^{-6} m^3/s
Feed composition:	
Gas	Y_A = 0.11 (molar);
MEA solution	C_B = 30 *wt. %*
Input feed temperatures	T_L=293 *K*; T_G=298 *K*
Density:	
CO2 (at 0 °C and 1 atm) [8]	ρ_{CO2}=1.963 kg/m^3
Gas mixture [9]	ρ_{gas} =Σ($y_i \cdot \rho_i$) kg/m^3
Aqueous alkanolamine solution [10]	$\rho = 2.45 \cdot C_{BO} + 919.13 \cdot e^{24.23/T_L}$ kg/m^3
CO_2 solubility according with Henry's law [10]	$H_{CO_2} = 10^{(5.3 - 0.035 \cdot C_{B0} - \frac{1140}{T_L})}$ $atm \cdot m^3/kmol$
Diffusion coefficient of CO_2 in water [10]	$D_{CO_2,w} = 2.35 \cdot 10^{-6} \cdot e^{\left(-\frac{2119}{T_L}\right)}$ m^2/s
Diffusion coefficient of CO_2 in amine solution [10,11]	$D_{CO_2,Am.sol} = D_{CO_2,w} \cdot \left(\frac{\mu_{H_2O}}{\mu_{MEA}}\right)^{\gamma}$ m^2/s
Diffusion coefficient of CO_2 in gas [9]	$D_{CO_2} = 1.38 \cdot 10^{-5} \cdot \left(\frac{p_o \cdot T}{p \cdot T_o}\right)^{3/2}$ m^2/s
Viscosity:	
MEA solution [9]	$\ln(\mu_{MEA}) = 0.16 \cdot C_{MEA} - 19.1 \cdot e^{\frac{298.3}{T_L}}$ $Pa \cdot s$
Thermal conductivity:	
CO_2 [8,9]*	λ_{CO2}=8·10^{-5}·T_G-0.0071 *W/m·K*
Air [8,9]*	λ_{air}=7·10^{-5}·T_G+0.005 *W/m·K*
Specific heat capacity *(J/kgK)*: $C_p = b \cdot T + cT^{-2} + a$	
MEA [8]	*a b c* 1411.264 4.7151 0
H_2O [9]	4185 0 0
CO_2 [8]	983.24 0.2605 -1.86·10^{-7}

the equation has been obtained via regression of data taken from literature

The partial differential equations of the mathematical model were transformed in ordinary ones, by discretization. The mathematical model was solved using MATLAB software package (version 2006) to evaluate the rate of CO_2 absorption changes with respect to the MEA concentration decrease in the aqueous solution.

For modeling and simulation of the carbon dioxide absorption in packed columns, the parameters presented in the Table 1 were used.

Model simulation results

The simulation of the mathematical model of CO_2 absorption into aqueous mono-ethanolamine solution show the evolutions (both in time and space) of temperature, and concentration in the liquid and gas phase, in the gas – liquid absorption column. Some of the most representative simulation results are presented in the figures below.

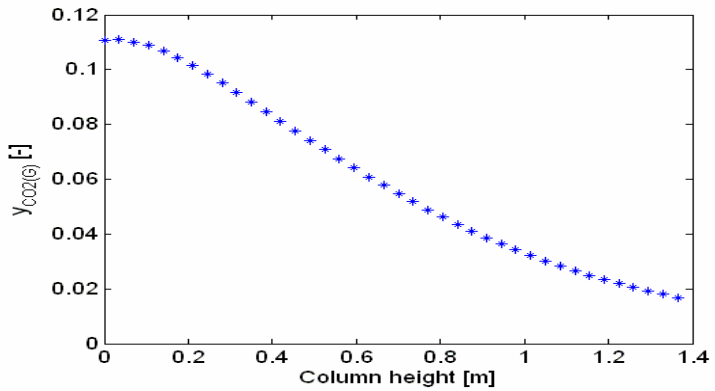

Figure 2. CO_2 concentration (in gas phase) along the column height

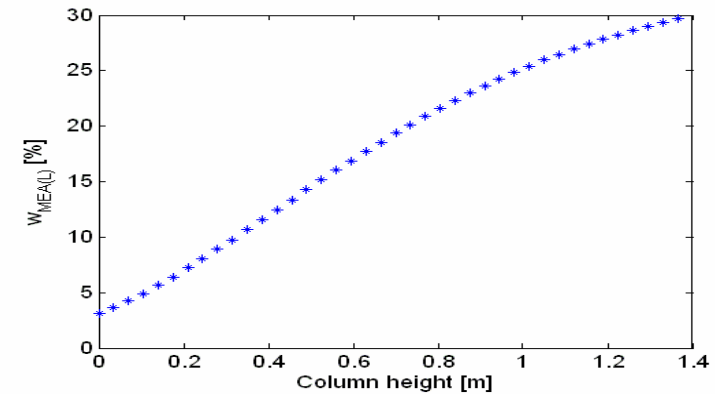

Figure 3. MEA concentration profile along the column height

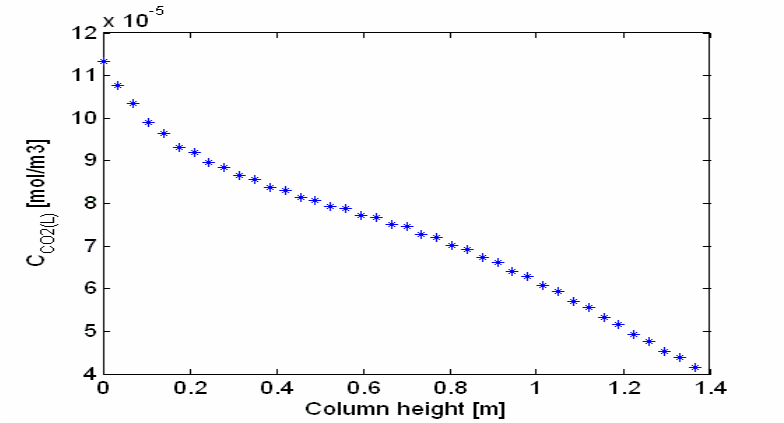

Figure 4. CO_2 concentration (in liquid phase) profile along the column height

In Figure 3 an increasing in the concentration of MEA in liquid phase respectively a decrease of CO_2 in gas and liquid phase against column height is observed. Because the rate of reaction is directly proportional to carbon dioxide concentration in the liquid phase and the concentration of MEA, the rate of reaction increases versus the column height. Figure 2 shows the decreasing of the CO_2 concentration in the gas phase due to the chemical absorption [12, 13].

The temperature profile along the column is presented in Figure 5 (chemical absorption of carbon dioxide is an exothermic process).

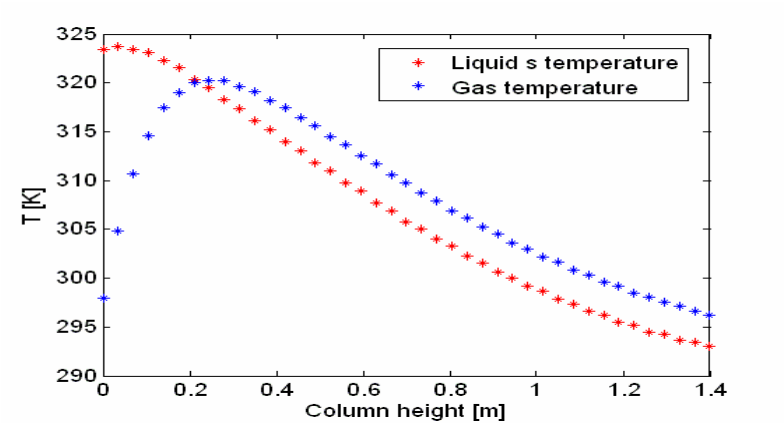

Figure 5. Temperature profile along the column height

The simulation results were compared with data collected from literature [3,12,14] and data obtained (by authors) from simulation of the CO_2 absorption process using ChemCAD, in the same operational conditions, in order to validate the application developed for modeling and simulation of the absorption process.

Table 2. Comparison of data obtained with developed model and ChemCAD software, $F_L=3{,}42\cdot10^{-6}$ m^3/s, $F_G=2\cdot10^{-3}$ m^3/s.

Parameter	MATLAB	CHEMCAD
Input Concentration of MEA in liquid phase [wt%]	30.00	30.00
Output Concentration of MEA in liquid phase [wt%]	3.11	2.64
Input molar fraction of CO_2 in gas phase [-]	0.110	0.110
Output molar fraction of CO_2 in gas phase [-]	0.0168	0.0100
Input temperature of the liquid flow [K]	293.00	293.00
Output temperature of the liquid flow [K]	323.40	324.78
Input temperature of the gas flow [K]	298	298
Output temperature of the gas flow [K]	296.20	296.76

The good correlation between the results of developed model and ChemCAD model data indicates the accuracy of developed chemical absorption model described above in predicting actual gas-absorption performance of absorption packed column.

The dynamic behavior of the absorption column was also investigated in the presence of the typical process disturbances (e.g. gas and liquid flow variation). Knowledge of the behavior in time to the occurrence of disturbance is important for the process control design and process optimization [9]. Some of the most representative results are presented in the Figures 6 to 8.

Figure 6 shows the effect of the liquid flow increasing on liquid flow's temperature when appear a perturbation. The temperature of the liquid flow at input, at the top of the column, is 293 K and it is increasing to 319.9 K at output, at the bottom, because of exothermic reaction (reaction heat is 65000 kJ/kmole).

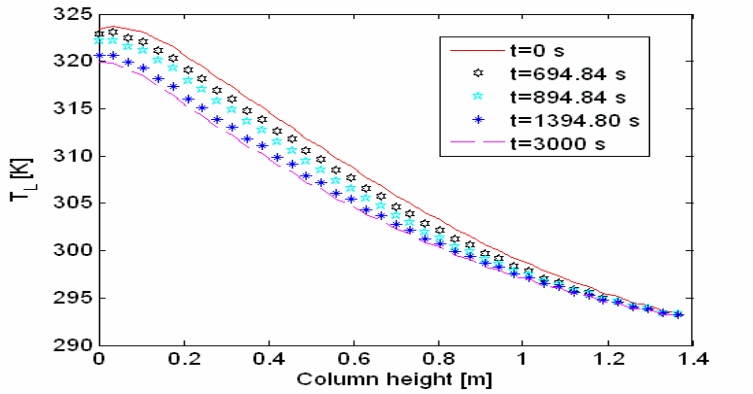

Figure 6. Variation of liquid's temperature ($F_L = F_L + 20$ %)

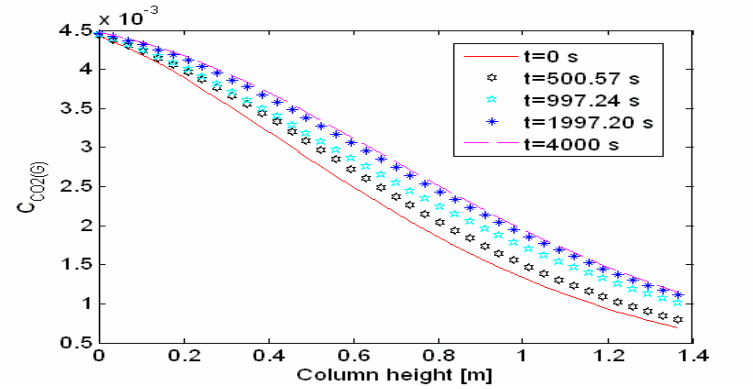

Figure 7. Variation of CO_2 molar fraction in gas phase (F_G=F_G + 20 %)

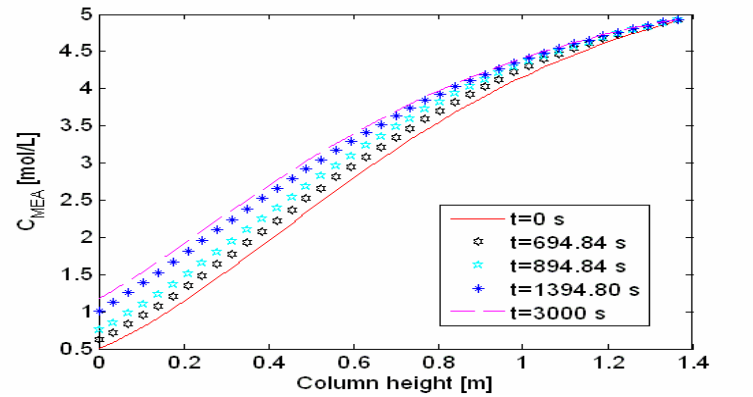

Figure 8. Variation of MEA height concentration ($F_L = F_L + 20$ %)

Figure 7 shows the effect of the gas flow increasing on CO_2 concentration in gas phase. The presence of process perturbations determine a significant increasing of CO_2 output concentration. Figure 8 shows the MEA concentration evolution in time and column's height if the liquid flow increasing. All these stationary and dynamic parameters profiles along the packed absorption column are valuable information for process optimization and to develop a control strategy for the process.

The developed mathematical model will be tuned against experimental data for adjusting the parameters and then it can be used for pre-screening and designing practical CO_2 absorption process in various conditions (laboratory, pilot and industrial size, different solvents and column internals, various operational conditions etc.).

CONCLUSION

A mathematical model was developed for analyzing carbon dioxide absorption rate and understanding of micro level interaction of various processes going inside de reactor (packed absorption column). Simulation of carbon dioxide gas – liquid absorption process in mono-ethanolamine (MEA) was done using Matlab software.

The evolutions of the process parameters (liquid and gaseous flows, composition of the streams, temperatures) were studied during the carbon dioxide absorption process. For verification of the developed model, the simulation results were compared with ChemCAD model simulation.

The mathematical model and the simulation results proved to be a reliable tool for process analyzing and are useful for making preliminary calculations of experimental parameters for the column absorption. Also, the developed model can be used to determine optimal operation conditions and to design the control system.

NOTATION

a_u	specific area (m^2/m^3)
A	gaseous reactant (CO_2)
b	stoichiometric coefficient of B
B	liquid reactant (MEA)
C_A	concentration of dissolved gas A ($kmol/m^3$)
C_{AG}	concentration of A in gas ($kmol/m^3$)
C_B	concentration of reactant B ($kmol/m^3$)
C_{B0}	initial concentration of reactant B ($kmol/m^3$)
$c_{p,CO2}$	specific heat capacity of CO_2 (J/mol*K)
$c_{p,G}$	specific heat capacity of gas (J/mol*K)
c_{psol}	specific heat capacity of solution (J/mol*K)

D	column's diameter (m)
$D_{CO2,i}$	diffusion coefficient of CO_2 in substance *i* (m2/s)
E	enhancment factor (-)
F_G	flow rate of gas (m^3/s)
F_L	flow rate of solution (m^3/s)
h	heat transfer coefficient in gas phase (J/s*m^2*K)
H	column's height (m)
H_{CO2}	Henry's constant [-]
k	reaction rate constant (m^3/mol·s)
k_L	liquid film mass transfer coefficient (m/s)
K_G	overall mass transfer coefficient (m/s)
p_o	normal pressure (1 atm)
t	time (s)
T_G	gas phase temperature (K)
T_L	liquid phase temperature (K)
T_o	normal temperature (273 K)
v_L	axial velocity of liquid film (m/s)
v_G	velocity of gas film (m/s)
y_{CO2}	molar fraction of CO_2 in gas (-)
z	axial coordinate (m)
$\Delta_r H$	heat of reaction (J/kmol)
ρ_g	density of gas (kg/m^3)
ρ_{sol}	density of solution (kg/m^3)
μ_i	viscosity of component *i* (Pa·s)

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