

Rate-Based Modelling and Validation of an Absorber and Stripper in an Amine-Based Post-Combustion CO₂ Capture Process

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Carbon emissions capture and storage is regarded as an essential approach to mitigate the greenhouse effect led by carbon dioxide emissions from the fossil fuels combustion. Amine-based post-combustion CO₂ capture technologies have great potential for retrofitting existing coal-fired power plants. In this paper, a mathematical model for a packed absorber and stripper in a CO₂ capture process are developed. Typical aqueous monoethanolamine (MEA) with 30 wt.% concentration is selected as the absorbent. A rate-based method is implemented to represent the mass and heat transfer in carbon dioxide absorption and desorption processes. In addition, the heat of CO₂ is derived by Gibbs-Helmholtz equation. In this way, the effect of chemical equilibrium and thermodynamic equilibrium on absorption capacity and absorption heat can be obtained. Finally, these models are validated by literature data in different plant operating conditions. The present mathematical models can be used to analyse the mass and heat transfer behaviour and to improve the overall performance of the CO₂ process.

1. Introduction

Carbon dioxide is regarded as the predominant greenhouse gas that leads to global warming. The Intergovernmental Panel on Climate Change (IPCC) claims that the massive emissions of carbon dioxide contribute over half of increased temperature in recent decades (Oliver, 2013). The main source of carbon dioxide emissions is fossil fuels combustion. Therefore, it is essential to integrate carbon capture technologies with the large-scale emission source, such as coal-fired power plants, to mitigate CO₂ emissions (Yaumi et al., 2017). Amine-based post-combustion CO₂ capture technology is considered as an effective way and owns a great potential for further commercial application (Wang et al., 2017).

Considering the energy consumption and operation flexibility, the simulation of post-combustion carbon capture process is necessary to study the feasibility for the real industrial application. Kvamsdal et al. (2009) developed a stand-alone CO₂ absorber model and used steady-state data of the temperature profiles, rich solvent loading and CO₂ capture rate from a pilot plant to validate the model. This work emphasized the necessity of the modelling the absorber to understand the complexities of real plant operation. Gaspar et al. (2012) set up a dynamic absorption/desorption model and also validated it by steady-state plant data. As the supplement and extension of the previous work, Gaspar et al. (2016) validated the model with the transient data in response to the flue gas flow rate changes in a pilot plant. Flø et al. (2015) set up a rate-based model of the CO₂ absorption process in Matlab and validated the model with steady-state and transient pilot plant data from the pilot plant in Norwegian University of Science and Technology. Manaf et al. (2016) utilized the system identification method with the transient pilot plant data to set up a black box model, instead of physical mechanism model. Zhao et al. (2017) used the equilibrium stage model in Aspen Plus to analyze the energy flow in the carbon capture process with different absorbent. According to this research, the aqueous MDEA solution with lower absorption heat is a better choice than typical MEA solution for the energy consideration. Montañés et al. (2017) developed a dynamic model based on conventional amine-based configuration, considering the size, geometry and materials of the key equipment. This model was validated steady state and dynamic plant data from the Technology

Centre Mongstad carbon capture plant. Bui et al. (2018) developed a dynamic model by the gCCS modules to study the interaction between the key process parameters, such as liquid to gas ratio and capture rate, during the dynamic amine-based carbon capture process.

In this paper, a rate-based model for a packed absorber and stripper is implemented in gPROMS. The typical solution, aqueous MEA with 30 wt.% concentration, is chosen as the absorbent in this model. The modeling method is introduced in section 2. To simplify the thermodynamic calculation, the equilibrium partial pressure of CO₂ is expressed by a function of temperature and carbon loading by Chen et al. (2011) approach. This equilibrium method was not used for overall performance calculation of absorber and stripper. The heat of CO₂ is derived by Gibbs-Helmholtz equation. Validation of the model is conducted by comparing the simulation results with the data from a pilot plant in section 3 and conclusions from this work are given in section 4.

2. Model development

A typical amine-based CO₂ absorption system mainly includes an absorber, a stripper, and a rich/lean heat exchanger (RLHX). The absorption/desorption process is presented in Figure 1. In this process, flue gas enters the absorber from the bottom and contacts with the countercurrent lean absorbent from the top of the absorber. The majority of CO₂ in flue gas is eliminated and vent gas exits from the top of the absorber. The rich solvent after absorption is preheated in the RLHX for heat recovery by the lean solvent at the bottom of the stripper. Then CO₂ in the rich solvent is regenerated during the desorption reaction in the stripper. Then the lean solvent is introduced to the top of the absorber to form a closed loop.

The absorber and stripper are the key equipment in the carbon capture process. The column is discretized along the height and the control volume contains vapor and liquid phase. The following assumptions are used in this model.

- Plug flow regime is considered in each control volume.
- Liquid and vapor phases are considered as ideal phases.
- Both columns are adiabatic.
- Mass and heat transfer are described by the two-film theory and rate-based model.
- Mass transfer of inert gas, such as N₂ and O₂, is negligible.
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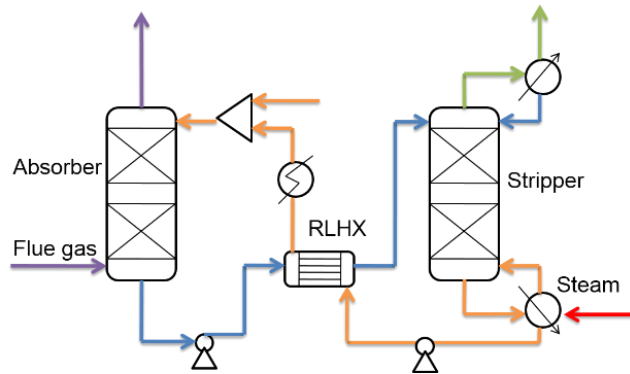


Figure 1: Flow diagram of a conventional CO₂ capture process

2.1 Conservation equations

Conservation equations are the main control equations in this model, including mass, component and energy balances. Mass and component conservation equations are described as follows:

$$0 = \frac{1}{A} u_s^L \frac{\partial c_{tot}^L}{\partial z} + \frac{1}{A} c_{tot}^L \frac{\partial u_s^L}{\partial z} + \sum_i J_i a_{pe} \quad (1)$$

$$0 = -\frac{1}{A} u_s^V \frac{\partial c_{tot}^V}{\partial z} - \frac{1}{A} c_{tot}^V \frac{\partial u_s^V}{\partial z} - \sum_i J_i a_{pe} \quad (2)$$

$$0 = \frac{1}{A} u_s^L \frac{\partial c_i^L}{\partial z} + \frac{1}{A} c_i^L \frac{\partial u_s^L}{\partial z} + J_i a_{pe} \quad (3)$$

$$0 = -\frac{1}{A} u_s^V \frac{\partial c_i^V}{\partial z} - \frac{1}{A} c_i^V \frac{\partial u_s^V}{\partial z} - J_i a_{pe} \quad (4)$$

where the subscripts i denote components H₂O and CO₂, superscripts L and V denote liquid and vapor phases respectively, c_{tot} is the total concentration of a phase, u_s is superficial velocity, J is mass transfer flux, a_{pe} is effective specific area of the packing between liquid and vapor phases for mass transfer, A is the interface area between liquid and vapor phases.

Energy conservation equations are described as follows:

$$0 = u_s^L \frac{\partial T^L}{\partial z} + \frac{h_{coeff} a_{pe}}{C_{pm}^L \rho^L} (T^v - T^L) + \frac{J_{CO_2} a_{pe}}{h_{LF} C_{pm}^L \rho^L} \Delta H_{abs} + \frac{J_{H_2O} a_{pe}}{h_{LF} C_{pm}^L \rho^L} \Delta H_{vap} \quad (5)$$

$$0 = -u_s^V \frac{\partial T^V}{\partial z} - \frac{h_{coeff} a_{pe}}{C_{pm}^V \rho^V} (T^V - T^L) \quad (6)$$

where T is temperature, h_{coeff} is the heat transfer coefficient between liquid and vapor phases, C_{pm} is the specific heat capacity on mass basis, ρ is density, ΔH_{abs} stands for the absorption heat of CO₂, ΔH_{vap} stands for the heat of vaporization of H₂O.

2.2 Mass transfer equations

Mass transfer for the components CO₂ and H₂O can be described by the two-film theory as Figure 2 shows. The transfer resistance consists of vapor and liquid resistance. The flux of mass transfer is calculated by the following equation:

$$J_i = K_i^{ov} (c_i^V - c_i^{L*}) \quad (7)$$

where the superscript * denotes the state of thermodynamic equilibrium, K_i^{ov} represents the overall mass transfer coefficient.

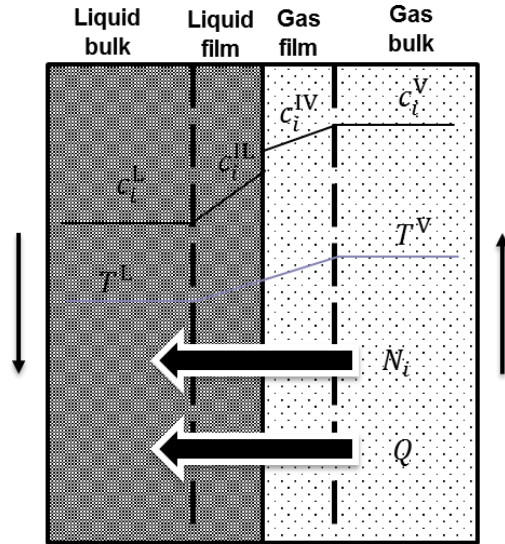


Figure 2: Illustration of the two-film model

The overall mass transfer coefficient for H₂O equals the mass transfer coefficient of the vapor phase side because the resistance of the vapor phase side is far more than that of liquid phase side. As for the component CO₂, the method of enhancement factor is used in rate-based model. The overall mass transfer coefficient is calculated by the following equation:

$$K_{CO_2}^{ov} = \frac{1}{\left(\frac{1}{K_{CO_2}^V} + \frac{H_{CO_2}}{EK_{CO_2}^L}\right)} \quad (8)$$

where H_{CO_2} is the Henry's constant, $K_{CO_2}^V$ and $K_{CO_2}^L$ represent the mass transfer coefficient in vapor and liquid phase respectively, E is the enhancement factor which presents the effect of the existence chemical reaction upon the absorption process. The mass transfer coefficient can be calculated by the correlations in previous literature (Onda et al., 1968; Bravo et al., 1992).

2.3 Thermodynamic equations

In this work, a semi-empirical thermodynamic equilibrium model is implemented to reduce the amount of calculation (Chen et al., 2011), as Equation 9 shows. In this model, the equilibrium partial pressure of CO_2 is assumed as a function of temperature T and solvent carbon loading α . Therefore, the calculation of activity coefficient can be avoided. The constants a, b, c, d, e are fitting coefficient for amines. In terms of the MEA, a, b, c, d, e equal to 36.61, -11152, -7.46, 2389, 26.69.

$$\ln P_{CO_2}^* = a + \frac{b}{T} + c\alpha + \frac{d\alpha}{T} + e\alpha^2 \quad (9)$$

Thereby, the expression of CO_2 absorption heat ΔH_{abs} is obtained by Gibbs-Helmholtz equation:

$$\Delta H_{abs} = -R \frac{d(\ln P_{CO_2}^*)}{d\left(\frac{1}{T}\right)} = -R(b + d\alpha) \quad (10)$$

where CO_2 absorption heat is a function of solvent carbon loading α .

3. Model validation

Feasibility of the above mathematical model needs to be tested by comparing simulation results and literature data. In this work, the practical operation data is selected from the pilot plant experiments in the University of Texas, Austin (Dugas, 2006). The information of the absorber and stripper is listed in Table 1. For the modelling verification, the main performance in experiments data need to be distribute in a relatively wide range. The following five typical cases in different working conditions are chose to validate the column model, in which the reboiler duty is from 30% to 100% based on case 1. The information of the working conditions in these cases is listed in Table 2.

Table 1: Main parameters for absorbers and strippers

	Unit	Absorber	Stripper
Operating pressure	bar	1.01	1.66
Packing type	-	IMTP	FLEXIPAC
Packing height	m	6.1	6.1
Column diameter	m	0.427	0.427

Table 2: Working conditions in different cases

	Unit	Case 1	Case 2	Case 3	Case 4	Case 5
CO_2 concentration in flue gas	vol.%	16.6	16.5	16.0	17.7	17.5
Flue gas temperature	$^{\circ}C$	55	48	54	47	53
Flue gas flow rate	m^3/h	660	660	660	330	330
Lean solvent carbon loading	mol/mol	0.278	0.290	0.231	0.279	0.284
Lean solvent temperature	$^{\circ}C$	40	40	40	40	40
Lean solvent flow rate	m^3/h	6.25	4.63	2.36	2.44	2.57
Rich solvent temperature	$^{\circ}C$	69	73	80	86	85
Reboiler duty	kW	469	366	209	152	155

Temperature profiles of the absorber and stripper are shown in Figure 3 and Figure 4 respectively. The simulation results are in accordance with the pilot plant data. Validation of simulation results of rich solvent carbon loading, CO_2 capture rate, lean solvent carbon loading are depicted in Figure 5. Similarly, the model calculation results are in line with the experimental data.

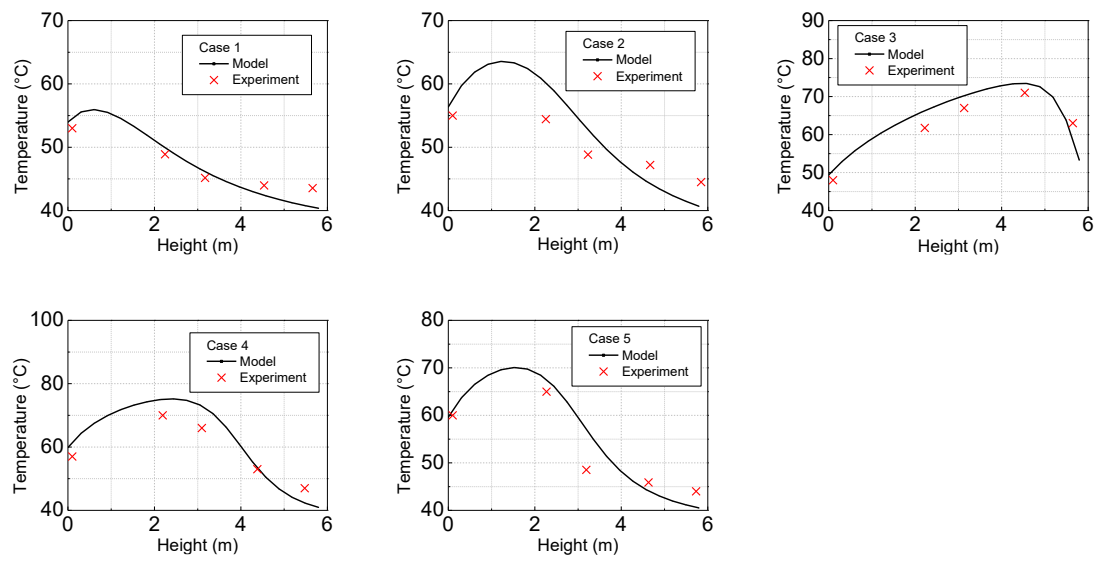


Figure 3: Temperature profiles of the absorber in different cases

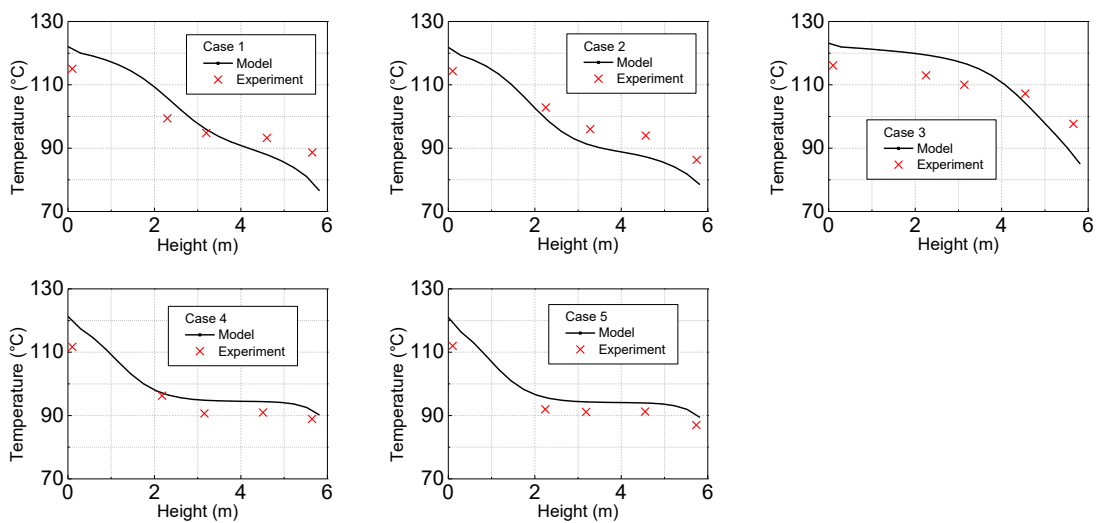


Figure 4: Temperature profiles of the stripper in different cases

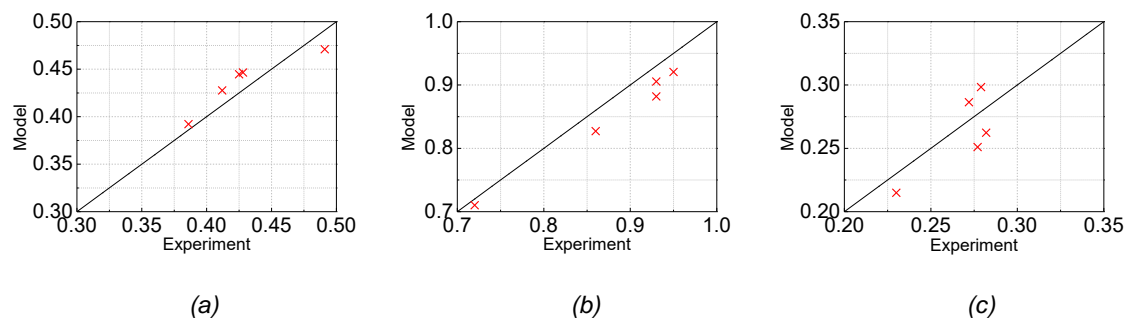


Figure 5: Validation of simulation results of rich solvent carbon loading (a), CO₂ capture rate (b), lean solvent carbon loading (c)

4. Conclusions

This paper developed a model for an absorber and stripper in the post-combustion CO₂ capture process based on the physical mechanism method. The control equations mainly consist of conservation, mass transfer and thermodynamic equations. A rate-based model based on the enhancement factor method is implemented to calculate the mass transfer flux. For maintain the flexibility and simplicity of the model, a semi-empirical model of equilibrium partial pressure of CO₂ is used in thermodynamic calculation. The equilibrium model correlates the CO₂ pressure with temperature and load and provides the heat of absorption required in the energy balance. Since the modelling approach doesn't include the rigorous electrolyte calculation, the electrolyte concentration distribution along the height of absorber and stripper cannot be reflected in this model. However, in terms of the overall performance calculation, such as carbon capture rate and carbon loading, the mathematical model for an absorber and stripper is feasible by the validation of the experimental data in different cases from a pilot plant. This work provides a foundation for further dynamic model development with an agreeable dynamic performance.

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