RATE BASED MODELING AND VALIDATION OF A CARBON-DIOXIDE PILOT PLANT ABSORBTION COLUMN OPERATING ON MONOETHANOLAMINE

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Abstract
In-silico amine screening is a fast, low-cost and promising way of efficiently evaluating new amine molecules which are proposed for carbon-dioxide capture purposes. In order to implement the screening environment, reliable and robust absorber models are required. This contribution presents the modeling and validation results of a CO_2 capture pilot absorber operated with monoethanolamine (MEA), as the first step of the in-silico solvent screening framework. The simulation results have shown that the outlet amine loading and CO_2 partial pressure can be predicted with a 10% deviation from the experimental values for one column, with larger deviations for the second. Note that no parameter fitting was performed and the model relies entirely on engineering and property correlations available in the scientific literature. In addition the model was extended to include the calculation of the overall mass transfer coefficient from laboratory based wetted-wall experiments completed at CSIRO. This further improved the model prediction and significantly reduced the prediction error for the other column.

Keywords: carbon-dioxide, rate based absorber column, pilot plant,

1. Introduction

CO_2 absorption is based on the reaction of CO_2 (weak acid) with an amine (weak base) during which a water soluble salt is formed[1]. A capture plant consists mainly of two equipment: the absorber and the desorber. These two columns are packed with either random or structured packing materials. A simplified flow sheet for the absorption process for CO_2 in an aqueous monoethanolamine (MEA) solution is showed in Figure 1. Before the flue gas enters the absorber, it is important to remove all SO_2 and NO_X in order to prevent the formation of unwanted nitrates and sulfates. The flue gas is fed into the absorber column at temperatures between 40 °C and 50 °C at a pressure of about one atmosphere. The liquid is fed into the absorber at the top of the column while the gas at the bottom. This work deals with the modeling of the absorber column. Other recent work has focused on the evaluation of several amines for absorption purposes[2], evaluation of absorption capacity[3] and chemical equilibrium related investigations[4].

2. Rate based model description

2.1 Material balances

The model is rate based and consists of a set of differential mass and energy balances, which are completed with a correlation that takes the systems pressure drop into account. The description of the gas-liquid interface is based on the two-film model and uses the following assumptions: the reaction takes place in the liquid film of the gas-liquid interface system; the liquid bulk is in equilibrium; since the liquid phase heat transfer resistance is small compared to that of the gas phase, the liquid interface temperature equals the liquid bulk temperature; the interfacial surface for heat and mass transfer is identical; axial dispersion is neglected; the absorption occurs adiabatically; and the mole fraction of dissolved but unreacted CO_2 is neglected. A simple thermodynamic model is used to describe the equilibrium reaction system with all non-idealities taken into account in a combined Henry's law and equilibrium constant. Several rate based model formulations are found in the literature e.g. rate based models implemented in the Aspen Custom Modeler environment[5] and the universal column model[6].
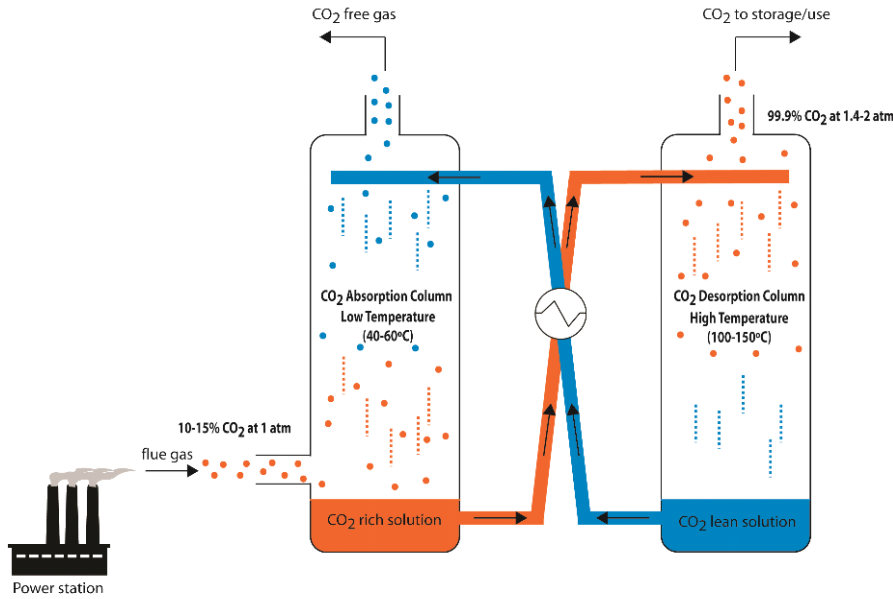
Figure 1. Gas absorption-desorption system

The system of differential equations for the model consisting of the mass and energy balances, taking into account the stoichiometric relations for the absorption, is described by Gabrielsen et al.[7] This model is completed by the addition of a differential equation describing the pressure drop.

2.2 Mass transfer through the interfacial area
The molar flux N of CO_2 over the interface is described by an overall gas side mass transfer expression:

$$N = K_G(p_{CO2} - p^*_{CO2})$$ (1)

where K_G is the overall gas side mass transfer coefficient of CO_2. p^*_{CO2} is the equilibrium partial pressure of CO_2 via a thermodynamic model. The equilibrium partial pressure of H_2O is calculated via an Antoine equation. In the two film theory, the overall mass transfer coefficient including gas and liquid side transfer resistance is expressed by:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{Ek^*_L}$$ (2)

where H and E are the appropriate Henry's law constant, and the enhancement factor respectively. k_G and k^*_L are the mass transfer coefficients without reaction in the gas and liquid phase respectively. Since the liquid consists mostly of water, the liquid side mass transfer resistance of H_2O can be neglected.

Several implicit and explicit equations to calculate the enhancement factor were trialed[8]. However, the equations (3) and (4) from Cussler[9] were chosen as they gave stable solutions with values similar the other equations tested:

$$E = \sqrt{M} \coth(\sqrt{M})$$ (3)

$$M = \frac{D_{CO2}r}{(k^*_L)^2}$$ (4)

where D_{CO2} is the diffusion coefficient of CO$_2$ in the liquid and r is the reaction rate. For an amine present in high concentration that is not depleted in the liquid film (pseudo-first-order behaviour) and that reacts rapidly with CO$_2$ to form a carbamate (as is the case for MEA) r is given by equation (5):

$$M = k_2 C_{MEA} \qquad\qquad (5)$$

where k_2 is the second-order reaction rate constant between MEA and CO$_2$ and C_{MEA} is the free MEA concentration.

The wetted interfacial area for mass and heat transfer and k_L^* was calculated according to the Billet-Schultes[10] and Onda[11] correlations with the Billet-Schultes correlation yielding more reasonable results.

2.3 Heat transfer through the interfacial area
In order to obtain the heat transfer coefficient in the gas phase, the Chilton-Colburn analogy is applied, the expressions for the analogy are taken from Bird et al[12]. The j factors for the analogies describe the dimensionless heat transfer and mass transfer. The heat of absorption is calculated using the equation and parameters derived by Gabrielsen et al[7]. The heat flux q between the liquid and the gas is given by the analogue flux correlation as for the mass transfer, using the temperature difference of gas (T_G) and liquid (T_L) phase as the driving force for the transfer:

$$q = h(T_G - T_L) \qquad\qquad (6)$$

2.4 Computational Implementation
The described model is implemented in MATLAB$^{®}$ version 7.4.0 and solved using the boundary value problem solver subroutine *bvp4c*, which uses a collocation method to solve the system of differential equations. The quality of the guesses is essential for the subroutine to be able to produce a solution or to converge at all. Non-convergence was observed when the initial guesses at intermediate locations in the column are not close to the solution. In order to ensure feasibility, initial simulations were carried out with relaxed tolerances of the solver. Once the model was solved with these settings, the resulting state variable vectors were used as initial guesses for a next simulation and the solver tolerances were tightened. This approach greatly improved the simulation of columns with unknown initial values of state variables.

3. Pilot columns and experimental data acquisition procedure
The pilot plant has two columns each with two 1.35 m packed sections consisting of 16 mm Pall rings and is located at the Loy Yang brown coal fired power station in Victoria's Latrobe Valley, Australia. For the data used in this work the columns were arranged in series using 30% w/w aqueous MEA as the absorbent. The liquid entered at the top of column 1 and the gas at the bottom of column 2. The carbon-dioxide mole fraction in the gas stream was 12%. The model is compared against measurement data which consists of the following parameters for the inlet and outlet streams:

liquid phase - CO$_2$ loading (mol CO$_2$ / mol MEA) and temperature
gas phase - CO$_2$ mol fraction, water mole fraction and temperature

Additionally, liquid and gas-phase temperature measurements were available between the column sections. The CO$_2$ loading in the liquid was determined by offline titration of liquid samples. The gas phase concentrations of CO$_2$ and H$_2$O were determined online using a Gasmet FTIR analyser. Temperature measurements were made using thermocouples directly in the columns.

4. Comparison of model output to pilot plant data
The column simulations using the mass transfer coefficient calculated according Equations 2-5 and existing literature correlations for all other data are presented in Figures 2-5. Circles represent pilot plant measurements.
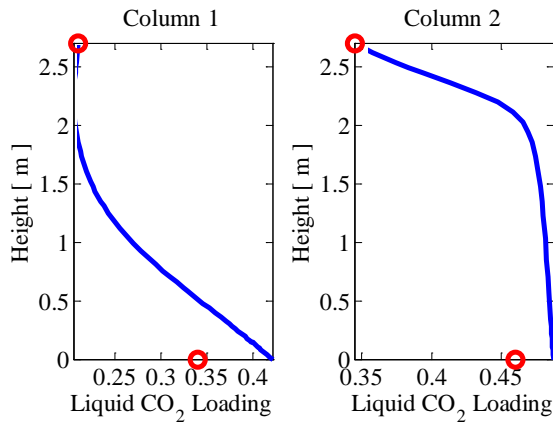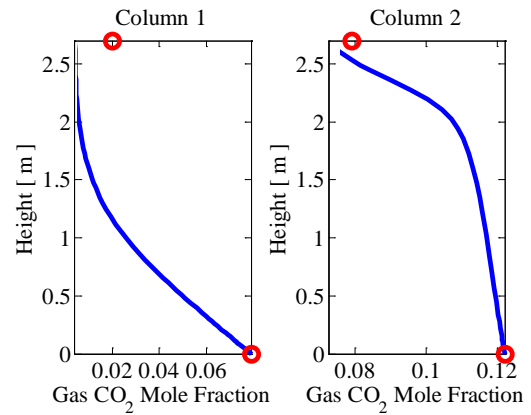
Column 1 Column 2 Column 1 Column 2

Figure 2. Liquid CO_2 loading - literature. **Figure 3.** Gas phase CO_2 - literature.
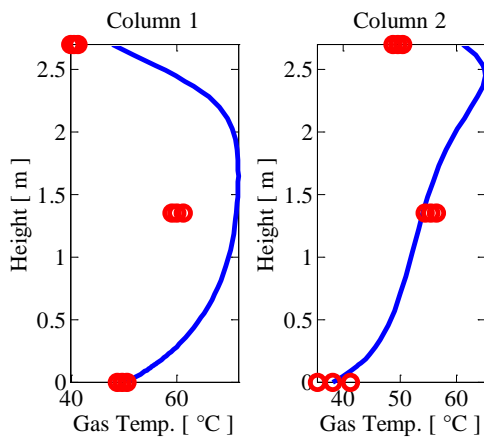
Column 1 Column 2 Column 1 Column 2

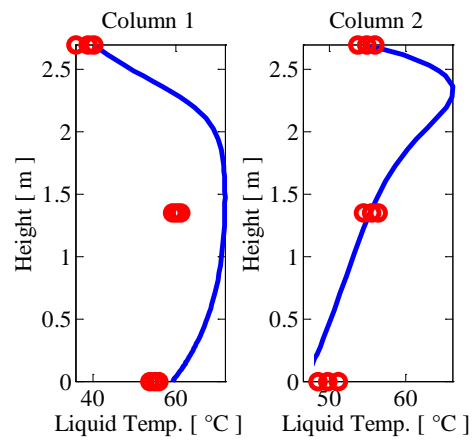**Figure 4.** Gas phase temperature - literature. **Figure 5.** Liquid phase temperature - literature.

The simulation results show that the outlet liquid CO_2 loading experimental values are matched within 10% by the model simulations for column 2. The agreement for column 1 is poor. Due to the liquid loading overestimation in both columns the gas phase CO_2 fraction is underestimated, as shown in Figures 2 and 3. The gas phase temperature prediction for column 1 is unsatisfactory; however the temperature profile for column 2 is in close agreement to the measurements. Overall the predictions for column 2 are in good agreement with the measurements but not for column 1.

The liquid phase measurements are matched better than the gas phase. A possible source for this is that the model assumes adiabatic conditions, and heat-loss to the atmosphere is not considered. Since the columns are not insulated this heat-loss may have an impact and its impact would be largest on the gas phase.

5. Extension of the model to estimate mass transfer from wetted-wall measurements

In previous work wetted-wall data of CO_2 mass transfer into 30% w/w aqueous MEA has been collected as a function of liquid CO_2 loading and temperature[13]. In order to incorporate this experimental mass transfer data into the model the liquid side mass transfer coefficient at a particular CO_2 loading and temperature was determined according to Equations 7-9 from Cussler[8]:

$$k_L = \sqrt{D_{CO2}r}\coth(\sqrt{\frac{D_{CO2}r}{(k_L^*)^2}}) \tag{7}$$

If the chemical reaction rate is much greater than k_L^* then $\coth(\sqrt{\frac{D_{CO2}r}{(k_L^*)^2}})$ =1. This condition is obeyed in the wetted-wall so for the wetted-wall the following equation holds:

$$k_{L,ww}(\alpha,T) = \sqrt{D_{CO2}(\alpha,T)r(\alpha,T)} \tag{8}$$

Defining Equation 7 in terms of the column and substituting Equation 8 into it yields:

$$k_{L,col}(\alpha,T) = k_{L,ww}(\alpha,T)\coth(\frac{k_{L,ww}(\alpha,T)}{k_{L,col}^*(T)}) \tag{9}$$

where $k_{l,ww}(\alpha,T)$ is the liquid side mass transfer coefficient at a particular loading (α) and temperature (T) measured using the wetted-wall, $k_{l,col}(\alpha,T)$ is the liquid side mass transfer coefficient at a particular loading and temperature estimated in the column, and $k_{L,col}^*(T)$ is liquid side mass transfer coefficient at a particular temperature in the column.

The advantage of this approach is that deviation from assumptions around pseudo-first-order behaviour in the liquid film are automatically captured in $k_{L,ww}$. $k_{l,ww}(\alpha,T)$ was determined by interpolating (using a cubic spline) curves of $k_{l,ww}$ as a function of loading to the required value of α. The values of $k_{l,ww}$ at α were then linearly interpolated or extrapolated by a small amount to the required temperature. The model simulation results based on mass transfer calculated using the wetted-wall experiments are presented in Figures 5-9.
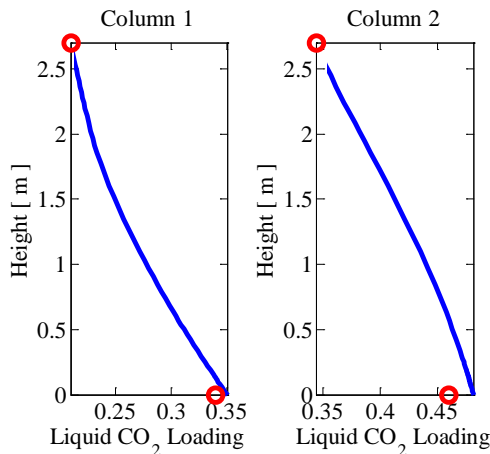

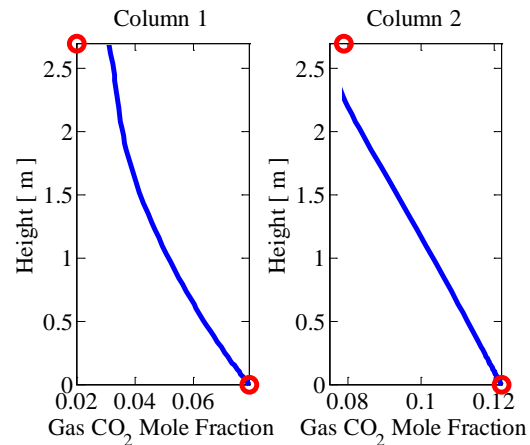**Figure 6.** Liquid CO₂ loading – wetted-wall.   **Figure 7.** Gas phase CO₂ – wetted-wall.

The simulation results using the mass transfer data from the wetted-wall experiments have shown improved model prediction capabilities, particularly for column 1. The prediction of the temperature in both the gas and liquid phase of column 2 is worse using literature mass transfer data but all other predictions are equivalent or improved. The current model formulation is based on the assumption that there is no axial dispersion which is a model simplification and is not a conclusion based on experimental observation.

6. Conclusions
The simulation results have shown that the outlet amine loading and CO₂ partial pressure can be predicted with a 10% deviation from the experimental values. The model was extended to include the calculation of the overall mass transfer coefficient from laboratory based wetted-wall experiments completed at CSIRO. This further improved the model prediction and significantly reduced the prediction error for the column 1. Note that no parameter fitting was performed on the pilot plant experimental data and the model relies entirely on engineering and property correlations available in

the scientific literature. Incorporation of heat loss related calculations should improve the prediction capabilities of the model. Eventually, the full predictive capability of the model will be concluded after tests on larger columns and after experiments using different amines.
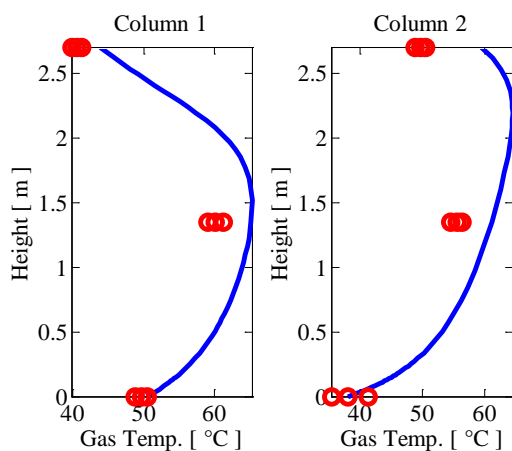

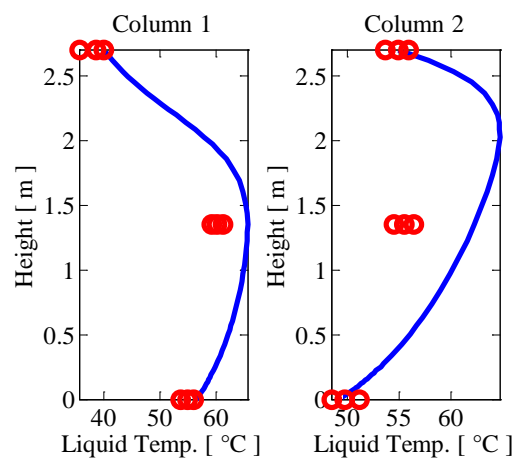**Figure 8.** Gas phase temperature - wetted-wall.

Figure 9. Liquid phase temperature - wetted-wall.

References
1. P. D. Vaidya et al., *Chem. Eng. Tech.,* 30(2007), 1467-1474
2. G. Puxty et al., *Environ. Sci. Technol.,* 43(2009), 6427-6433
3. N. McCann et al., *Ind. Eng. Chem. Res.,* 47(2008), 2002-2009
4. N. McCann et al., *J. Phys. Chem. A,* 113(2009), 5022-5029
5. L. Kucka et al., *Chem. Eng. Sci.,* 58(2003), 3571-3578
6. B. Huepen et al., *Ind. Eng. Chem. Res.,* 49(2009), 772-779
7. J. Gabrielsen et al., *AIChE J.,* 52(2006), 3443-3451
8. R. M. Wellek et al., *Can. J. Chem. Eng.,* 56(1978), 181-186
9. E. L. Cussler, *Diffusion – Mass Transfer in Fluid Systems*, Cambridge University Press (2009)
10. R. Billet et al., *Chem. Eng. Res. Des.,* 77(1999), 498-504
11. K. Onda et al., *AIChE J.,* 5(1959), 235-239
12. R. B. Bird et al., *Transport phenomena*, John Wiley & Sons, Inc (2002)
13. G. Puxty et al., *Chem. Eng. Sci.,* 65(2010), 915-922