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Equilibrium Stage Mathematical Model of the Chemical Absorption of CO2 into Monoethanolamine (MEA) Aqueous Solution

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Abstract
This paper presents an equilibrium stage mathematical model to optimize the operating conditions to remove CO_2 from flue-gases using MonoEthanolAmine (MEA) aqueous solution in a stage column. For the modeling, the absorption column is divided into a number of segments assuming that liquid and gas phases are well mixed. The number of stages of the column is assumed as a model parameter while temperature and composition profiles and flow-rates of the aqueous solution and gas streams along the column are considered as optimization variables.
The proposed model is implemented in GAMS (General Algebraic Modeling System) and CONOPT is used as NLP solver.
The influence of main process operating conditions the inlet gas and aqueous amine solution conditions (composition, temperature and flow-rates) and number of trays or height equivalent to a theoretical plate (HETP) on the absorption performance is investigated. Detailed discussion of the optimization results are presented through different case studies.

Keywords: Post-combustion CO_2 Capture, Optimization, Equilibrium Stage Mathematical Model.

1. Introduction
Coal and natural gas will continue to contribute a large proportion of the world's commercial energy in the near future. It is expected that 90% of the energy system will be supplied by fossil fuels in 2030. Consequently, technologies of CO_2 emissions reduction are necessary in order to prevent the global warming of the earth.
This paper deals with the modeling and optimization of the post-combustion CO_2 capture process. Precisely, an equilibrium stage mathematical model is developed to optimize the operating conditions to remove CO_2 from flue-gases in a stage column.

2. Problem statement
Given the flue gas conditions (composition, temperature and flow-rate), the goal of the optimization problem is to determine the optimal operating conditions in order to maximize the absorption efficiency. The objective function is defined as the ratio between the total absorbed CO_2 and the flow-rate of amine aqueous solution.
Temperature, composition and flow-rates profiles of aqueous solution and exhaust gas streams along the absorber are optimized simultaneously. The influence of the main model parameters such as the number of trays on the absorption performance is also investigated.

3. Hypothesis and mathematical model
In this section, the adopted hypothesis and the mathematical model for the entire process are presented.

Assumptions
The mathematical model was developed on the basis of following assumptions:
a. Equilibrium Stages are assumed. Liquid and vapor phases are well-mixed.
b. Dependence of stage efficiency with gas and liquid velocities and enhancement factor, among others, is considered
c. Dependence of the reaction heat with CO_2 loading and temperature is considered.
d. Murphree efficiencies for CO_2 and H_2O in each stage are considered.
e. Ideal behavior in the liquid phase.
f. Real behavior in the vapor phase. Fugacity coefficients are computed by using Peng-Robinson equations of state for multi-components.
g. CO_2 and water can only be transferred from liquid phase to vapor phase and vice-versa.
h. Vaporization of the amine is neglected.

i. Reactions take place in liquid phase.
j. Dependence of aqueous alkolamine solution density with the temperature is taken into account.
l. The following reactions are considered:

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad \text{(R1)}$$

$$2H_2O + CO_2 \leftrightarrow H_3O^+ + HCO_3^- \quad \text{(R2)}$$

$$H_2O + HCO_3^- \leftrightarrow H_3O^+ + CO_3^{2-} \quad \text{(R3)}$$

$$H_2O + MEAH^+ \leftrightarrow H_3O^+ + MEA \quad \text{(R4)}$$

$$MEAH + HCO_3^- \leftrightarrow H_2O + MEACOO^- \quad \text{(R5)}$$

$$MEA + CO_2 + H_2O \leftrightarrow MEACOO^- + H_3O^+ \quad \text{(R6)}$$

Mathematical model.
By adopting the mentioned assumptions and based on the Fig. 1, the following mathematical model was derived.

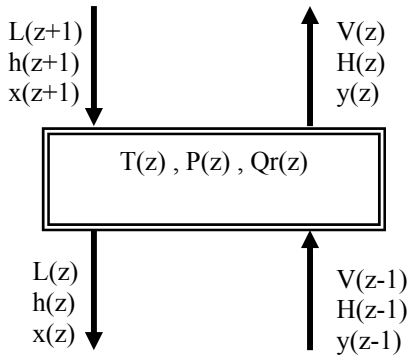

Figure 1. Schematic stage "z"

Overall mass balance in stage z:

$$L_{z+1} - L_z + V_{z-1} - V_z = 0 \quad (1)$$

L(z+1) and V(z-1) are the liquid and vapor molar flows entering to the stage z while L(z) and V(z) are the liquid and vapor molar flows leaving the stage.
Species mass balance in stage z:

$$L_{z+1}x_{iz} - L_z x_{iz} + V_{z-1}y_{jz-1} - V_z y_{jz} = 0 \quad (2)$$

xi and yj refer to the mole fraction of component "i" in liquid and vapor phases, respectively.

$$\sum y_{jz} = 1 \qquad j = CO_2, H_2O, N_2, O_2 \quad (3)$$

$$\sum x_{iz} = 1 \quad i = CO_2, H_2O, MEA, MEAH^+, MEACOO^-, HCO_3^-, H_3O^+, OH^- \quad (4)$$

Energy balance in stage z:

$$L_{z+1}h_z - L_z h_z + V_{z-1}H_{z-1} - V_z H_z + \Delta H_R - \Delta H_{H2O} = 0 \quad (5)$$

where H and h are enthalpies of vapor and liquid respectively. ΔH_R and ΔH_{H2O} refer respectively to the reaction heat released and vaporization heat of water [1, 2]

Chemical equilibrium constants:

$$K_m = \prod_i (a_{iz})^{v_i} = \prod_i (x_{iz}\gamma_{iz})^{v_i} = a + (b/T) + c\ln(T) + dT \quad (6)$$

where K_m refer to the chemical equilibrium constants of reactions R1 to R5. T is absolute temperature (K). a_{iz} , γ_{iz}, v_i are activity, coefficient activity and estequiometric coefficient to component "i" in reaction "m" respectively. Liquid phase has ideal behavior, therefore the activity coefficients are considered equal to one (Kent-Eisenberg model).

Phase equilibrium relationship:

$$y_{CO_2 z}\varphi_{CO_2 z}P_z = H_{CO_2 z}[CO_2]_z \quad (7)$$

$$y_{H_2O\,z}\varphi_{H_2O\,z}P_z = p_{H_2Oz}[H_2O]_z \quad (8)$$

where $[i]_z$ is the molar concentration of specie "i" in stage "z". (φ) , P_z and p_{H_2Oz} refer to fugacity coefficient, total pressure and partial pressure of water, respectively.

Charge balance in stage z:

$$[MEAH^+]_z + [H_3O^+]_z = [MEACOO^-]_z + [HCO_3^-]_z + 2[CO_3^{2-}]_z + [OH^-]_z \quad (9)$$

Ionic mass balance relationship in stage z:

$$\alpha[MEA]_z^0 = [CO_2]_z + [MEACOO^-]_z + [HCO_3^-]_z + 2[CO_3^{2-}]_z \quad (10)$$

The superscript (0) means initial condition. CO_2 loading (α) is defined as the ratio between total CO_2 and total amine.

Murphree efficiency:

$$\eta_z = \frac{V_z y_{iz} - V_{z-1} y_{iz-1}}{V_z y_{iz}^* - V_{z-1} y_{iz-1}} \quad (11)$$

Enhancement factor

The Enhancement factor is given by equation (12). It may be considered as a correction to the liquid-side mass transfer coefficient due to pseudo- first order reaction.

$$E_z = \frac{\sqrt{D_{CO_2}\left(k_{r,CO2-MEA}[MEA] + k_{r,CO2-OH}[CO_2]\right)}}{k_L} \quad (12)$$

Effective area for mass transfer

$$a = \frac{a_w}{a_t} = 1 - \exp\left(-1.45\left(\frac{\sigma_c}{\sigma}\right)^{0.75}\left(\frac{L}{a_t\,\mu^L}\right)^{0.1}\left(\frac{L^2\,a_t}{(\rho^L)^2\,g}\right)^{-0.05}\left(\frac{L^2}{\rho^L\sigma\,a_t}\right)^{0.2}\right) \quad (13)$$

where σ μ^L, μ^G a_t u^G A σ refer, respectively, to surface tension, liquid and gas viscosities, specific dry area of packing, superficial gas velocity, cross-sectional area of column.

The proposed model was implemented in General Algebraic Modeling System GAMS [3]. The generalized reduced gradient algorithm CONOPT 2.041 was here used as NLP solver [4]. Global optimal solutions can not be guaranteed due to the presence of bilinear terms and logarithms which introduce non-convexities into the mathematical model.

4. Applications of the NLP models

In this section, the validation of the proposed models and optimization results are discussed through Example 1 and 2, respectively. All solutions have been obtained by using Intel Core 2 Quad Extreme QX9650 3 GHz 1333 MHz processor and 4 GB RAM.

4.1. Model Validation.

The validation of the proposed model was conducted by comparing the output results of the model to those reported by [5] and also with results obtained by a process simulator (HYSYS).

Table 1. Model parameters used for validation

	Flue gas	Lean amine
Temperature (K)	316.15	314.15
Total flow-rate (Kmol/h)	26647	22478
CO_2 % mass	34.25	1.52
MEA % mass	0	18
H_2O % mass	0.7	80.48
N_2 % mass	65.75	0
Pressure (KPa)	1818.78	-

Table 2. Model parameters used for validation

Column Type	Packed
Diameter (m)	2.44
Total packing height (m)	24.15
Stages number	10
Packing specifications	
Type of packed	Ceramic Intalox Saddles
Specific area (m^2/m^3)	195
Nominal packing size (m)	0.05
Void fraction	0.8

Table 1 lists the model parameters related to the gas and amine conditions (temperature, composition and pressure) while in Table 2 are shown the parameter values corresponding to the absorber unit.

Figure 2 to 5 compare the temperature, flow-rate and composition profiles along the absorber obtained by using the proposed model and HYSYS. From these figures, it can be seen a good agreement between the values predicted by the proposed model and HYSYS.

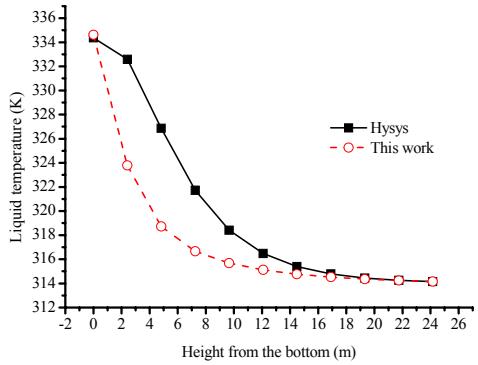

Figure 2. Liquid temperature vs. Height from the bottom. (Validation)

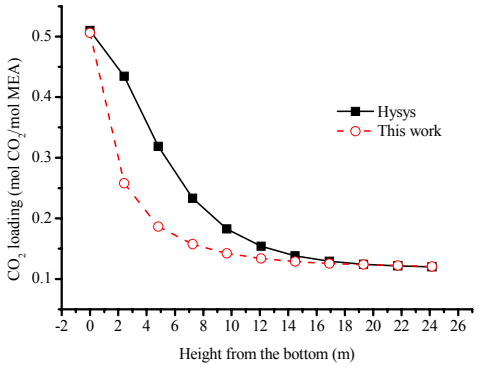

Figure 3. CO_2 loading vs. Height from the bottom. (Validation)

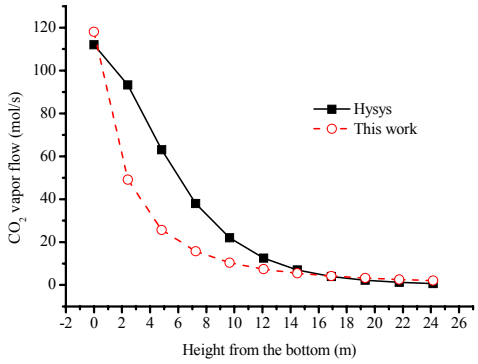

Figure 4. CO_2 vapor flow-rate vs. Height from the bottom. (Validation)

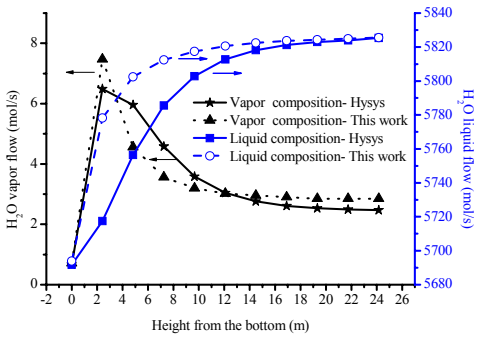

Figure 5. H_2O vapor flow-rate vs. Height from the bottom. (Validation)

Finally, Table 3 compares the main process parameters obtained from: (a) proposed model, (b) HYSYS simulator and (c) data reported by [5].

Table 3. Results validation

	Design data [Alatiqui et al. (1993)]	Hysys	This work
Gas exit			
Temperature (K)	316	314.25	314.24
CO_2 mol fraction	-	1.20E-03	3.50E-03
H_2O mol fraction	4.80E-03	4.38E-03	4.80E-03
Liquid exit			
Temperature (K)	334	334.37	334.62
CO_2 loading	0.481	0.5098	0.5060
CO_2 recovery (%)	-	99.631	98.925

According to the comparison, it is posible to conclude that output conditions of both streams (liquid and gas) are also in agreement with those obtained by HYSYS and [5].

2. Example 2. Optimization Problem

As mentioned in Section 2, the proposed mathematical model is used to obtain the optimal operating variables in order to recover the maximum CO_2 contained in flue gases by using the minimum flow-rate of amine solution.
The inlet gas conditions used are listed in Table 1. The influence of the absorber height as well as the CO_2 composition on the flue gas on the efficiency performance is investigated.
Inlet CO_2 concentrations of 3.73 % and 4.48%, 30 wt % of MEA aqueous solution are considered.
Optimal values obtained by varying the model parameters are shown from Fig. 6 to 11.
Precisely, Fig. 6 and 7 show the variation of OF with the inlet amine temperature and CO_2 loading, respectively. From Fig. 6, it can be seen that OF linearly decreases with increasing the CO_2 loading for a given inlet temperature of amine (313 K). The inlet temperature of amine has a slight influence on the OF (Fig. 7) for given CO_2 loading factors (0.15 and 0.20).

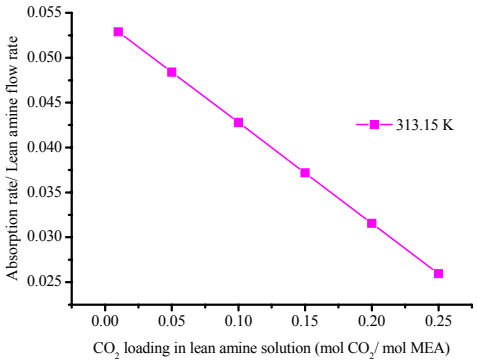

Figure 6. Optimal OF values vs. CO_2 loading.

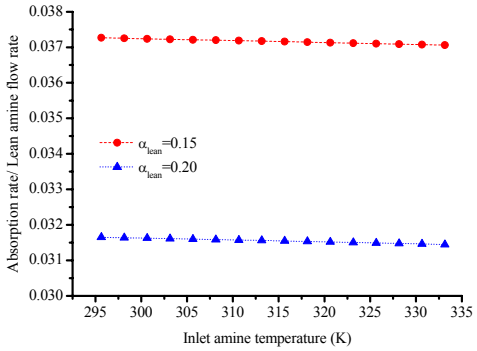

Figure 7. Optimal OF values vs. amine inlet temperature

Figure 8 shows that for lower CO_2 loading factor than 0.2, both amine flow-rate and CO_2 recovery increase with the increasing of the amine inlet temperature and it can clearly observed that a maximum CO_2 recovery is reached for αlean=0.2 and amine inlet temperature of 313.15 K. For αlean=0.15 the CO_2 recovery continuously increases with the inlet temperature.

As was expected, Fig. 9 clearly shows that the CO_2 recoveries increase with the decreasing of the CO_2 loading independently of the amine inlet temperature. In contrast to this, the lean amine flow rate increases as the amine inlet temperature increases.

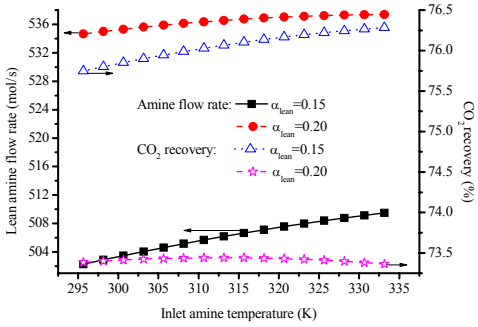

Figure 8. Amine flow-rate and CO_2 recovery vs. amine inlet temperature

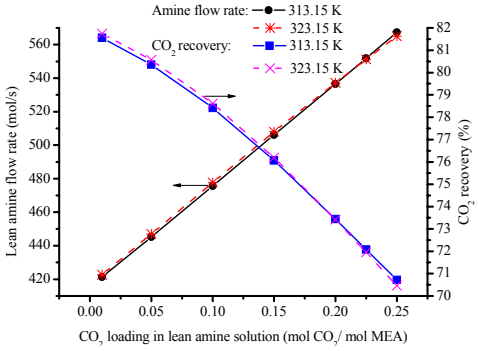

Figure 9. Amine flow-rate and CO_2 recovery vs. CO_2 loading

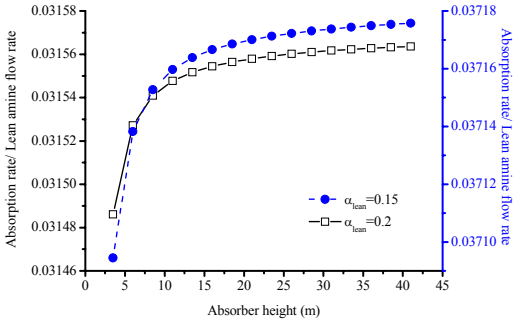

Figure 10. OF vs. absorber height

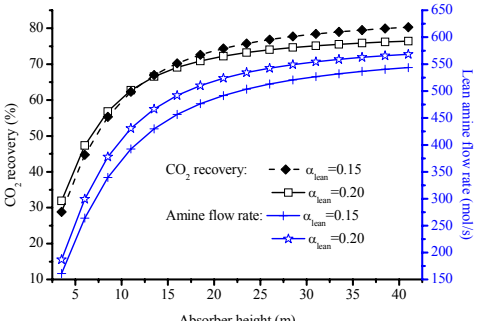

Figure 11. CO_2 recovery and amine flow-rate vs. absorber height

Finally, the influence of the absorber height on the optimal values corresponding to OF, amine solution flow-rate and CO_2 recovery are presented in Fig. 10 and 11. As was expected, the process efficiency defined by the OF increases with the increasing of the absorber height (Fig. 10). Higher absorber heights lead to higher CO_2 recovery and lean amine flow-rate (Fig. 11).

Acknowledgements

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