Supplementary Information for Sustainable Energy & Fuels

Mass Transfer Characteristics and Energy Penalty Analysis of MEA Regeneration Process in Packed Column

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1. Correlative terms

1.1. Mass transfer model source term

S_{CO2_G}(kg/m³/s) is the mass desorbed from the liquid phase per unit volume and time. The regeneration reaction of MEA is a second-order reaction, and S_{CO2_G}(kg/m³/s) can be expressed as follows[1,2]:

$$S_{CO_2\_G} = M_{CO2} \cdot k_r \cdot X_{MEACOO^-} X_{MEAH^+} \tag{1}$$

where M_{CO2} (kg/kmol) is CO_2 molecular weight; X_{MEACOO^-}(kmol/m³) and X_{MEAH^+}(kmol/m³) are the molar concentration of MEACOO⁻ and MEAH⁺ in the rich solution, respectively. k_r(kmol/m³/s) represents the reaction rate constant of the MEA regeneration reaction, which can be obtained by the Arrhenius equation[1]:

$$k_r = \frac{4.3 \times 10^{11}}{60} e^{\frac{E}{RT}} \tag{2}$$

where E (J/mol) is the activation energy of -8.079×10^4 J/mol. R(J/mol/K) represents the ideal gas constant.

S_{H2O_G}(kg/m³/s) is the mass of H_2O evaporating from liquid to gas phase per unit volume and time, which can be expressed as follows: [3,4]

$$S_{H_2O\_G} = k_{g,H_2O} a_w \left(p_{H_2O} - p_{H_2O,G} \right) M_{H_2O} \tag{3}$$

where $p_{H2O,G}$(kPa) is the partial pressures of H_2O in the main gas phase. $k_{g,H2O}$(kmol/kPa/m^2/s) is the gas phase mass transfer coefficient of H_2O, which can be obtained as follows:[3-5]

$$k_{g,H_2O} = \frac{5.23*(\frac{G_M}{a_T\mu_g})^{0.7}(\frac{\mu_g}{\rho_g D_{gH_2O}})^{\frac{1}{3}}(a_T d_p)^{-2}(\frac{D_{L,w}a_T}{R_g T})}{3600*101.325} \tag{4}$$

where G_M (kg/m^2/h) and μ_g(Pa·s) are the gas phase mass velocity and viscosity, respectively.

p_{H2O} (kPa) is the saturated vapor pressure of the water, which can be expressed as Antoine equation:

$$p_{H_2O} = 10^{(7.07406-1657.46/(746.13))} \tag{5}$$

As the losing mass of H_2O is equal to the adding mass of H2O in the gas phase, the source term of S_{H2O}(kg/m^3/s) can be expressed as follows:

$$S_{H_2O} = -S_{H_2O\_G} \tag{6}$$

S_{MEA^-}(kg/m^3/s) and S_{MEA}(kg/m^3/s) represent the MEACOO$^-$ consuming mass and MEA generation mass in the liquid phase as the reaction happening. Therefore, S_{MEA^-} and S_{MEA}(kg/m^3/s) can be expressed as follows:

$$S_{MEA^-} = -\frac{S_{CO_2\_G}}{M_{CO_2}}M_{MEACOO^-} \tag{7}$$

$$S_{MEA} = 2\frac{S_{CO_2\_G}}{M_{CO_2}}M_{MEA} \tag{8}$$

where M_{MEACOO^-} (kg/kmol) and M_{MEA} (kg/kmol) are MEACOO$^-$ and MEA molecular weights.

S_m (kg/m^3/s) is the source term of continuity equation, which is the losing mass of CO_2 and H_2O per unit volume and time, which can be expressed as follows:

$$S_m = -S_{CO_2\_G} - S_{H_2O\_G} \tag{9}$$

The packing materials of Mellapak type are investigated in this paper, which get widely used in industrial engineering. The liquid phase volume fraction h can be expressed as follows:[6]

$$h = ca_T^{0.83}L_{\mathrm{m}}^{x}\left(\mu_L/\mu_{L,0}\right)^{0.25}/100 \tag{10}$$

where a_T(1/m) is the surface area packings and L_{m}(m³/m²/h) is the volume flow rate of the rich solution. μ_L and $\mu_{L,0}$ (Pa·s) are the liquid phase viscosity and that at the temperature of 20℃. When L_{m} <40, c=0.0169, x=0.37. On the other hand, c=0.075, x=0.59.

The viscosity of rich solutions can be obtained from the empirical formula proposed by Weiland et al.[7]:

$$\frac{\mu_L}{\mu_{\mathrm{H_2O}}} = \exp\left(\frac{C_{\mathbf{MEA}}(21.186C_{\mathbf{MEA}}+2373)\left[r_{\mathbf{C}}\left(0.01015C_{\mathbf{MEA}}+0.0093T-2.2589\right)+1\right]}{T^2}\right) \tag{11}$$

where r_{C} (molCO₂/molMEA) is the CO₂ loading in the rich solution. μ_{H2O} (Pa·s) is the pure water viscosity.

The viscosity of pure water can be determined by the following correlation[8]:

$$\mu_{\mathrm{H_2O}} = 1.18\times10^{-6}\exp\left(\frac{16400}{RT}\right) \tag{12}$$

The MEA molecular diffusivity in the rich solutions can be calculated according to the empirical formula by Snijder et al.[9]:

$$D_{L,\mathrm{MEA}} = \exp\left(-13.275-\frac{2198.3}{T}-0.078142X_{\mathrm{MEA}}\right) \tag{13}$$

As reported by Versteeg and Vanswaaij, the molecular diffusivities of MEAH⁺ and MEACOO⁻ equal that of MEA[10].

1.2. Momentum equation source term

The interface drag force $\boldsymbol{F}_{LG}$ (N/m³) by the gas phase can be expressed as follows [11]:

$$F_{LG} = \frac{\Delta p_L}{|U_{slip}|} U_{slip} \tag{14}$$

where Δp_L(N/m³) is the pressure drop of the packing column. U_{slip} (m/s) represents the slip velocity between the gas and liquid phases, with the following formula calculated:

$$\mathbf{U}_{slip} = \mathbf{U}_G - \mathbf{U} \tag{15}$$

where $\mathbf{U}_G$(m/s) is the velocity vector of gas phase, and $\mathbf{U}$ (m/s) represents the liquid phase velocity vector.

The pressure drop of packing columnΔp_L(N/m³) can be obtained by the formula proposed by Robbins[12].

$$\Delta p_L = 0.774 \left(\frac{L_f}{20000} \right)^{0.1} \left(p_1 G_f^2 \times 10^{p_2 L_f} \right)^4 \tag{16}$$

where p_1=0.04002, p_2=0.0199, L_f (kg/m²/s) and G_f (kg/m²/s) are the liquid and gas loading factors, which can be obtained as follows:

$$G_f = G \left(1.2 / \rho_G \right)^{0.5} \left(F_{pd} / 65.62 \right)^{0.5} \tag{17}$$

$$L_f = L \left(1000 / \rho \right) \left(F_{pd} / 65.62 \right)^{0.5} \mu^{0.2} \tag{18}$$

The resistance by the packing materials can be gained by the empirical formula from Ergun and Orning[13].

$$F_{LS,x} = -\left(150 \mu \frac{(1-\gamma)^2}{\gamma^2 d_e^2} + 1.75 \rho \frac{(1-\gamma)}{\gamma d_e} |\mathbf{U}| \right) U \tag{19}$$

$$F_{LS,r} = -\left(150 \mu \frac{(1-\gamma)^2}{\gamma^2 d_e^2} + 1.75 \rho \frac{(1-\gamma)}{\gamma d_e} |\mathbf{U}| \right) V \tag{20}$$

where d_e (m) is the equivalent diameter of the packing, with the following form calculated:

$$d_e = \frac{6(1-\gamma)}{a_T} \tag{21}$$

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1.3. Energy equation source term

S_{T_G}(J/m³/s) is the energy equation source term of gas phase, which contains the physical volatilization heat of CO_2 and H_2O, the convective heat transfer. Therefore, S_{T_G} can be expressed as follows[14,15]:

$$S_{T\_G} = h_{\mathrm{exc}}a_w\left(T - T_G\right) + \frac{S_{CO_2\_G}}{M_{CO_2}}\cdot H_1 + \frac{S_{H_2O\_G}}{M_{H_2O}}\cdot H_2 \qquad (22)$$

where h_{exc}(w/m²/K) is the coefficient of convective heat transfer, which can be expressed as the Chilton–Colburn analogy[4]. a_w(m²/m³) represents gas and liquid contact area. H_1(J/kmol) is CO_2 volatilization heat, which is 1.975×10^7J/kmol. H_2(J/kmol) is water volatilization heat, which is 4.4×10^7J/kmol.

S_{T_L}(J/m³/s) is the energy equation source term of the liquid, which contains the regeneration reaction absorbing heat and the convective heat with gas.

$$S_{T\_L} = -\frac{S_{CO_2\_G}}{M_{CO_2}}\cdot H_R - S_{T\_G} \qquad (23)$$

where H_R is the endothermic chemical reaction heat, which is 8.4443×10^7J/kmol.

2. Boundary conditions

It is of significance for solving all the conservation equations to determine the real boundary conditions in the stripper, which is shown in Fig. 1. The detail settings of the boundary conditions for all of the conservation equations are presented in this part.

(1) The top of stripper.

Both the rich solution inlet and the gas phase outlet are at the top of the stripper. The boundary condition of the top is set as the velocity inlet in the Fluent 6.3.26. The boundary conditions of the top for each conservation equation are presented as follows:
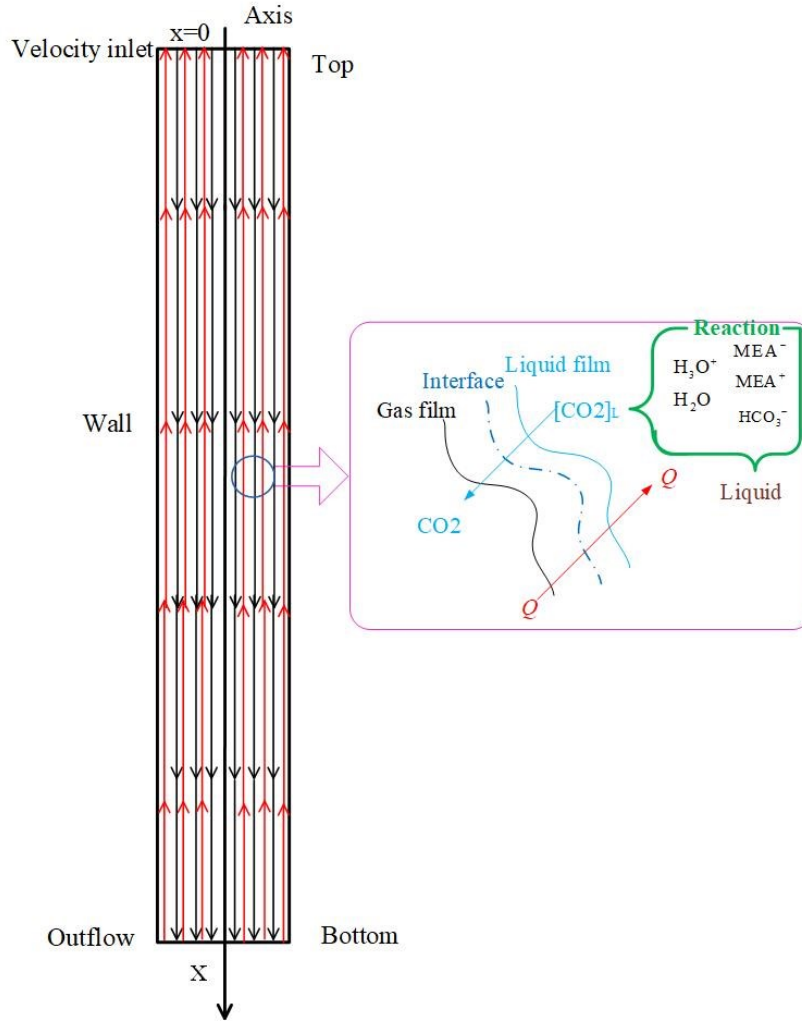
Fig. 1. Schematics of the regeneration process in the stripper and corresponding

boundary conditions.

The continuity equation:

$$U = U_{inlet} \tag{24}$$

$$V_{inlet} = 0 \tag{25}$$

The turbulent model:

$$k_{inlet} = 0.003 \cdot (U_{inlet})^2 \tag{26}$$

$$\varepsilon_{inlet} = \frac{0.09 \cdot (k_{inlet})^{1.5}}{d_H} \tag{27}$$

where d_H represents the hydraulicdiameter, which can be obtained as follow:

$$d_{\mathrm{H}} = \frac{\gamma}{\alpha_{\mathrm{T}}(1-\gamma)} \tag{28}$$

The energy conservation equation:

$$T = T_{\mathbf{inlet}} \tag{29}$$

$$\overline{t_{\mathbf{inlet}}^2} = (0.082\Delta T)^2 \tag{30}$$

$$\varepsilon_{t,\mathbf{inlet}} = 0.4 \cdot \left(\frac{\varepsilon_{\mathbf{inlet}}}{k_{\mathbf{inlet}}}\right) \overline{t_{\mathbf{inlet}}^2} \tag{31}$$

For the convenience, ΔT is set as 0.1K.

The mass fraction of i species (MEACOO⁻, MEA and H_2O) conservation equation:

$$C_i = C_{i,\mathbf{inlet}} \tag{32}$$

$$\overline{c_{\mathbf{inlet}}^2} = (0.082 C_{i,\mathbf{inlet}})^2 \tag{33}$$

$$\varepsilon_{c,\mathbf{inlet}} = 0.4 \cdot \left(\frac{\varepsilon_{\mathbf{inlet}}}{k_{\mathbf{inlet}}}\right) \overline{c_{\mathbf{inlet}}^2} \tag{34}$$

(2) The bottom of stripper:

The stripper bottom is designed for the outlet of the lean solution and the inlet of the gas phase. Because the fully developed condition of the rich solution can be achieved at the bottom of stripper, the outflow boundary condition in the Fluent 6.3.26 is set. The inlet temperature of gas phase is also set at this place. The boundary conditions of the bottom for each conservation equation are presented as follows:

The bottom is the outlet for the liquid phase. Owing to the outflow condition, a zero diffusion flux is achieved for all flow variables (Φ), which is presented as follows:

$$\frac{\partial \Phi}{\partial n} = 0 \tag{27}$$

The continuity equation: the inlet velocity of gas phase is input by the UDF (user define function).

The energy conservation equation:

$$T_G = T_{G,\text{inlet}} \tag{28}$$

The mass fraction of k species (CO_2 and H_2O) conservation equation:

$$C_k = C_{k,\text{inlet}} \tag{29}$$

(3) The wall of stripper:

The no-slip condition with the standard wall functions in the Fluent 6.3.26 is selected at the wall, owing to the advantage of the no-slip condition. Because the adiabatic column is assumed, the no heat transferred through the wall.

(4) The axis of stripper:

The hydraulic, heat and mass transfer characteristics are assumed to axis-symmetrical, so the axis condition is selected. Owing to the axis condition, the zero normal gradients of all variables (Φ) is achieved at the axis, which is presented as follows:

$$\frac{\partial \Phi}{\partial r} = 0 \tag{30}$$

3. Model verification

This model is verified by the regeneration experiments carried out by Tobiesen et al.[16], who reported nineteen groups of liquid phase temperature profiles in the packed columns. The stripper is equipped with Sulzer Mellapak 250Y packings. And the main information is presented in Table 1. Two runs of the experimental results are compared with the simulated data, which are shown in Fig.2. Fig.2 illustrates that the numerical data presents a good agreement with the experimental data. There are some small differences in Fig.2, which can be accepted. Therefore, the model in this paper is reliable enough to simulate MEA regeneration process in the packed columns.

Table 1

Detailed information of the experiment.

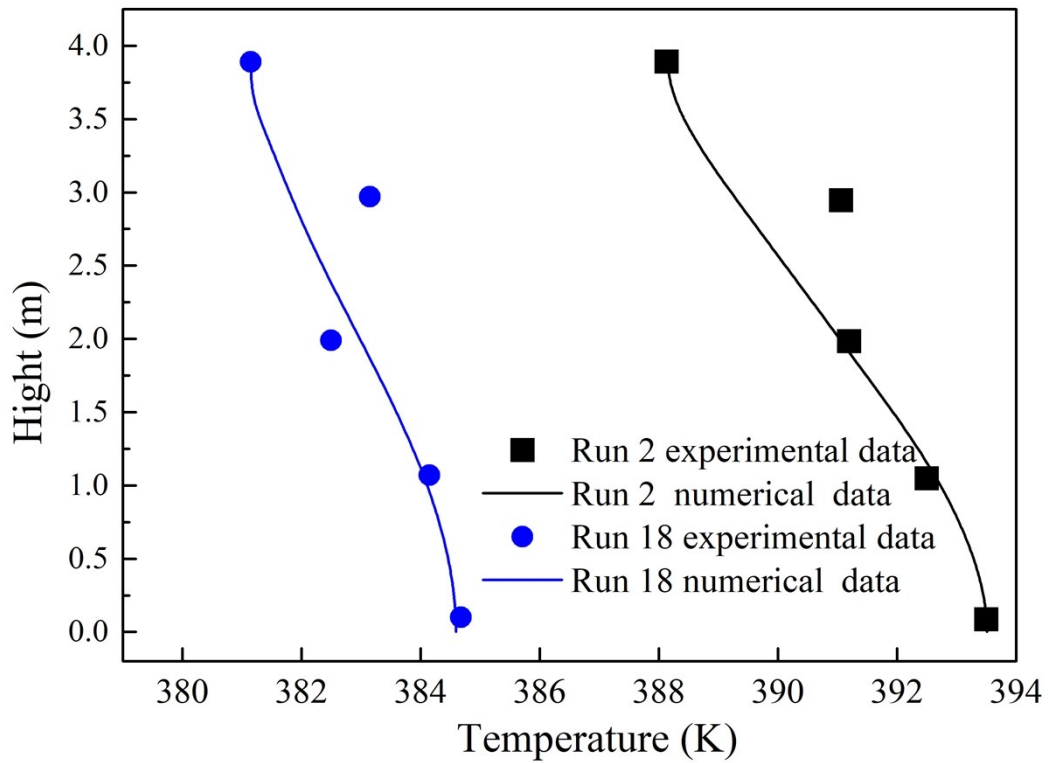|	Run 2	Run 18
Stripper hight(m)	3.89	3.89
Stripper diameter(m)	0.1	0.1
Gas flow rate (m³/h)	150	150
Liquid flow rate (m³/(m²·h))	7.64	17.20
MEA concentration (kmol/m³)	5.0	5.2
CO_2 loading (mol/mol)	0.315	0.407
Liquid inlet temperature (℃)	115	113

Fig. 3. Comparisons between numerical and experimental results.

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