

Model Development, Validation, and Part-Load Optimization of a MEA-Based Post-Combustion CO₂ Capture Process Under Steady-State Flexible Capture Operation

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Supporting Information for Publication

MODEL EQUATIONS FOR PACKED COLUMN

The steady-state molar balance of components in the vapor and liquid phase is given by eqs S1 and S2. In eq S2, superscript ‘a’ denotes apparent species as the chemical reactions occurring in the liquid phase produce true species that are denoted by superscript ‘t’.

Molar component balance for the vapor and liquid bulk

$$\frac{\partial(u_V C_{i,V})}{\partial z} = -N_{i,V}, \quad \forall i \in \{\text{CO}_{2(g)}, \text{H}_2\text{O}_{(g)}, \text{N}_{2(g)}, \text{O}_{2(g)}\} \quad (\text{S1})$$

$$\frac{\partial(u_L C_{i,L}^a)}{\partial z} = -N_{i,L}, \quad \forall i \in \{\text{CO}_{2(aq)}, \text{H}_2\text{O}_{(l)}, \text{MEA}_{(aq)}\} \quad (\text{S2})$$

Enthalpy balance for the vapor and liquid phase

The steady-state enthalpy balance over a differential element assuming negligible ambient heat loss and negligible axial dispersion of heat is given by eq S3 for the vapor and eq S4 for the liquid phases.

$$\frac{\partial(u_V C_{tot,V} \hat{C}_{p,V} T_V)}{\partial z} = Q_V \quad (\text{S3})$$

$$\frac{\partial(u_L C_{tot,L} \hat{C}_{p,L} T_L)}{\partial z} = Q_L \quad (\text{S4})$$

Transfer rate equations

The heat and mass transfer rates are described by eqs S5 to S13, where Q_V is the vapor film convective heat transfer term as defined in eq S5 and h'_V is the corrected heat transfer coefficient necessary for large mass transfer fluxes (Pandya 1983, Taylor et al. 1993). Q_L is defined as given in eq S6.

$$Q_V = h'_V a_e (T_L - T_V) \quad (\text{S5})$$

$$Q_L = Q_V + N_{\text{CO}_2,V} \Delta H_{abs} - N_{\text{H}_2\text{O},V} \Delta H_{vap} \quad (\text{S6})$$

$$h'_V a_e = \frac{\hat{C}_{p\text{CO}_2,V} N_{\text{CO}_2,V} + \hat{C}_{p\text{H}_2\text{O},V} N_{\text{H}_2\text{O},V}}{1 - \exp\left(-\frac{\hat{C}_{p\text{CO}_2,V} N_{\text{CO}_2,V} + \hat{C}_{p\text{H}_2\text{O},V} N_{\text{H}_2\text{O},V}}{h_V a_e}\right)} \quad (\text{S7})$$

The specific molar flux of the diffusing components across the interface is described using the two-film model as given by eq S8-S11.

$$N_{i,V} = k'_{V,i} a_e P (y_i - y_i^*), \quad k'_{V,i} = \frac{k_{V,i}}{RT_V}, \quad i \in \{CO_2, H_2O\} \quad (S8)$$

$$y_{H_2O}^* = x_{H_2O}^* \gamma_{H_2O}^* \frac{P_{H_2O}^{sat}}{P} = x'_{H_2O} \gamma_{H_2O} \frac{P_{H_2O}^{sat}}{P} \quad (S9)$$

$$y_{CO_2}^* = \frac{y_{CO_2} + \frac{\psi C_{CO_2,L}^t}{P}}{1 + \frac{\psi}{He_{CO_2}}}, \quad \psi = \left(\frac{Ek_{L,CO_2}}{k'_{V,CO_2}} \right) \quad (S10)$$

$$C_{CO_2,L}^* = \frac{y_{CO_2}^* P}{\gamma_{CO_2} He_{CO_2}} \quad (S11)$$

$$y_i = \frac{C_{i,V}}{C_{tot,V}}, \quad C_{tot,V} = \sum_i C_{i,V} = \rho(T_V, P, y_i) \quad \forall i \in \{CO_2, H_2O, N_2, O_2\} \quad (S12)$$

$$x_i^a = \frac{C_{i,L}^a}{C_{tot,L}}, \quad C_{tot,L} = \sum_i C_{i,L}^a = \rho(T_L, P, x_i), \quad \forall i \in \{CO_2, MEA, H_2O\} \quad (S13)$$

MODEL EQUATIONS: REBOILER

Molar component balance

$$F_{L,reb,in} x_{i,reb,in} - F_{L,reb,out} x_{i,reb,out} - F_{V,reb,out} y_{i,reb,out} = 0 \quad (S14)$$

$$\sum_i x_{i,reb,out} = 1, \quad \sum_i y_{i,reb,out} = 1 \quad (S15)$$

Energy balance

$$\dot{Q}_{reb} + F_{L,in} H_{L,in} = F_{V,reb,out} H_{V,reb,out} + F_{L,reb,out} H_{L,reb,out} \quad (S16)$$

$$\dot{Q}_{reb} = U_o A_{reb} (T_{steam} - T_{L,reb,out}) \quad (S17)$$

$$\dot{Q}_{reb} = \dot{m}_{steam} \Delta H_{steam} \quad (S18)$$

MODEL EQUATIONS: CONDENSER

Molar component balance

$$F_{V,cond,in} y_{i,cond,in} - F_{L,cond,out} x_{i,cond,out} - F_{V,cond,out} y_{i,cond,out} = 0 \quad (\text{S19})$$

$$\sum_i y_{i,cond,out} = 1, \quad \sum_i x_{i,cond,out} = 1 \quad (\text{S20})$$

Energy balance

$$\dot{Q}_{cond} + F_{V,in} H_{V,in} = F_{V,cond,out} H_{V,cond,out} + F_{L,cond,out} H_{L,cond,out} \quad (\text{S21})$$

MODEL EQUATIONS: PLATE HEAT EXCHANGER

While more details can be found in our previous publication (Akula et al., 2019), here is a summary of the equations:

Sub-HX Equations	Hot side(Lean solvent)	Cold side(Rich solvent)
Energy Balance	$T_{h,out}^i = T_{h,in}^i - \frac{\varepsilon_i \dot{C}_{\min}^i (T_{h,in}^i - T_{c,in}^i)}{\dot{C}_h^i}$	$T_{c,out}^i = T_{c,in}^i + \frac{\varepsilon_i \dot{C}_{\min}^i (T_{h,in}^i - T_{c,in}^i)}{\dot{C}_c^i}$
Capacitance rate	$\dot{C}_h^i = \frac{\dot{m}_h C_{p,h}}{NC_i}$	$\dot{C}_c^i = \frac{\dot{m}_c C_{p,c}}{NC_i}$
Minimum capacitance	$\dot{C}_{\min}^i = \min(\dot{C}_c^i, \dot{C}_h^i) \approx 0.5 \left(\dot{C}_c^i + \dot{C}_h^i - \left[(\dot{C}_c^i - \dot{C}_h^i)^2 + \delta_1 \right]^{0.5} \right)$	
Maximum capacitance	$\dot{C}_{\max}^i = \max(\dot{C}_c^i, \dot{C}_h^i) \approx 0.5 \left(\dot{C}_c^i + \dot{C}_h^i + \left[(\dot{C}_c^i - \dot{C}_h^i)^2 + \delta_2 \right]^{0.5} \right)$	
Capacitance ratio	$\bar{C}_{R,i} = \frac{\dot{C}_{\min}^i}{\dot{C}_{\max}^i}$	
Effectiveness	$\varepsilon_i = \begin{cases} \varepsilon_{c,i} (\text{P is EVEN}) = \begin{cases} \frac{1 - \exp[-NTU_i (1 - \bar{C}_{R,i})]}{1 - \bar{C}_{R,i} \exp[-NTU_i (1 - \bar{C}_{R,i})]}, & \bar{C}_{R,i} < 1 \\ \frac{NTU_i}{NTU_i + 1}, & \bar{C}_{R,i} = 1, \end{cases} \\ \varepsilon_{p,i} (\text{P is ODD}) = \frac{1 - \exp[-NTU_i (1 + \bar{C}_{R,i})]}{1 + \bar{C}_{R,i}} \end{cases}$	
Number of Transfer Units	$NTU_i = \frac{U_i A_p}{\dot{C}_{\min}^i}$	
Change of pass Boundary Condition	$T_{h,out}^i = T_{h,in}^{i+1}, \quad i = 1, \dots, P-1$	$T_{c,in}^i = T_{c,out}^{i+1}, \quad i = 1, \dots, P-1$
Inlet Boundary conditions	$T_{h,in}^i = T_{h,IN}, \quad i = 1$	$T_{c,in}^i = T_{c,IN}, \quad i = P$
Channel mass flow velocities	$G_{c,i}^h = \frac{\dot{m}_h}{bwNC_i}$	$G_{c,i}^c = \frac{\dot{m}_c}{bwNC_i}$
Port mass flow velocities	$G_{\text{port}}^h = \frac{4\dot{m}_h}{\pi d_{\text{port}}^2}$	$G_{\text{port}}^c = \frac{4\dot{m}_c}{\pi d_{\text{port}}^2}$
Pressure drop applied to both sides	$\Delta P = \left(\frac{2f(L + d_{\text{port}})PG_c^2}{\bar{\rho}d_h} \right) + 1.4 \left(P \frac{G_{\text{port}}^2}{2\bar{\rho}} \right) + \bar{\rho}g(L + d_{\text{port}})$	

Heat transfer coefficient	$h_i^h = \left(\frac{\lambda_i^h}{d_h}\right) a_1 (\text{Re}_i^h)^{a_2} (\text{Pr}_i^h)^{a_3}$	$h_i^c = \left(\frac{\lambda_i^c}{d_h}\right) a_1 (\text{Re}_i^c)^{a_2} (\text{Pr}_i^c)^{a_3}$
Overall heat transfer coefficient	$\frac{1}{U_i} = \frac{1}{h_i^h} + \frac{\delta_p}{\lambda_p} + \frac{1}{h_i^c}$	

PROPERTIES OF CO₂-MEA-H₂O SYSTEM

THERMODYNAMIC PROPERTIES

Molar volume

Vapor phase (ideal)

$$V_v = \frac{RT_v}{P} \quad (\text{S22})$$

Liquid phase

Pure solvent molar volume (m³/mol). T is temperature in kelvin.

$$V_s^\circ = \frac{M_s}{a_s T^2 + b_s T + c_s}, \quad s \in \{\text{MEA}, \text{H}_2\text{O}\} \quad (\text{S23})$$

Table S1: Pure molar volume parameters (Morgan et al. 2015)

Solvent, s	a_s	b_s	c_s	M_s
MEA	-5.35162×10^{-1}	-4.51417×10^2	1.19451×10^6	61.08
H ₂ O	-3.2484	1.65×10^3	7.93×10^5	18.02

Liquid mixture molar volume

Correlation by Weiland et al. (1998)

$$V_L = x_{\text{MEA}} V_{\text{MEA}}^\circ + x_{\text{H}_2\text{O}} V_{\text{H}_2\text{O}}^\circ + x_{\text{CO}_2} V_{\text{CO}_2} + x_{\text{MEA}} x_{\text{H}_2\text{O}} V^* \quad (\text{S24})$$

Correlation by Morgan et al. (2015)

$$V_L = x_{\text{MEA}} V_{\text{MEA}}^\circ + x_{\text{H}_2\text{O}} V_{\text{H}_2\text{O}}^\circ + v_1 x_{\text{CO}_2} + (v_2 + v_3 x_{\text{MEA}}) x_{\text{MEA}} x_{\text{H}_2\text{O}} + (v_4 + v_5 x_{\text{MEA}}) x_{\text{MEA}} x_{\text{CO}_2} \quad (\text{S25})$$

Table S2 : Parameters for Liquid mixture molar volume

Parameter	Value
V_{CO_2}	4.7470×10^{-8}
V^*	-1.8218×10^{-6}
v_1	1.02074×10^{-5}
v_2	-2.2642×10^{-6}
v_3	3.0059×10^{-6}
v_4	2.0700×10^{-4}
v_5	-5.6337×10^{-4}

Specific Heat capacity

Vapor Phase (J/mol K)

$$C_p^{ig} / R = a_0 + a_1 T + a_2 T^{-2} \quad (\text{S26})$$

T is temperature in kelvin. R is gas constant.

Table S3: Ideal gas heat capacity of vapor phase components(Smith 1950)

Component i	a_0	a_1	a_2
CO ₂	5.457	1.045×10^{-3}	-1.157×10^5
H ₂ O	3.47	1.45×10^{-3}	1.21×10^4
N ₂	3.28	5.93×10^{-4}	4.0×10^3
O ₂	3.639	5.06×10^{-4}	-2.27×10^4

Liquid Phase (J/mol K)

$$C_{p,i}^L = M_i (C_1 + C_2 t + C_3 t^2 + C_4 t^3 + C_5 t^4), \quad i \in \{\text{MEA}, \text{H}_2\text{O}\} \quad (\text{S27})$$

Where t is the temperature in degree Celsius and M is the molecular weight in g/mol.

Table S4: Specific heat capacity of solvent species (Hilliard 2008)

solvent	M_i	C_1	C_2	C_3	C_4	C_5
MEA	61.08	2.6161	3.706×10^{-3}	3.787×10^{-6}	0.0	0.0
H ₂ O	18.02	4.2107	-1.696×10^{-3}	2.568×10^{-5}	-1.095×10^{-7}	3.038×10^{-10}

Heat of vaporization of water

$$\Delta_{\text{vap}} H_{\text{H}_2\text{O}} = c_1 (1 - T_r)^{(c_2 + c_3 T_r + c_4 T_r^2)} \quad T_r = \frac{T}{T_c}; \quad T_c = 647.096 \text{ K} \quad (\text{S28})$$

where T is temperature in kelvin.

Table S5: Parameters for heat of vaporization of water (J/mol K)

C_1	C_2	C_3	C_4
5.66×10^4	0.61204	-0.6257	0.3988

Heat of absorption

A constant heat of absorption and desorption is assumed in the absorber and stripper respectively.

$$\Delta H_{\text{absorption}} = -84 \text{ kJ/mol}, \quad \Delta H_{\text{desorption}} = -97 \text{ kJ/mol} \quad (\text{S29})$$

Vapor Pressure

$$\ln(p_i^v) = A + \frac{B}{T_L} + C \ln T_L + D T_L^2 \quad i \in \{ \text{H}_2\text{O} \} \quad (\text{S30})$$

Table S6: Vapor pressure parameters for water (Pa)

	A	B	C	D
H ₂ O	72.55	-7206.7	-7.1385	4.05×10^{-06}

Henry's constant

Henry's constant (He_{CO_2} in Pa · m³/mol) using N₂O analogy (Jiru et al. 2012)

$$\begin{aligned}
 He_{CO_2} &= \exp\left(w_{MEA} \ln(He_{CO_2,MEA}) + w_{H_2O} \ln(He_{CO_2,H_2O}) + w_{MEA} w_{H_2O} \alpha_{MW}\right) \\
 \alpha_{MW} &= 1.70981 + 0.03972(T_L - 273.15) - 4.3 \times 10^{-4} (T_L - 273.15)^2 - 2.20377 w_{H_2O} \\
 w_{MEA} &= \frac{x_{MEA} M_{MEA}}{x_{MEA} M_{MEA} + x_{H_2O} M_{H_2O}}, w_{H_2O} = 1 - w_{MEA} \\
 He_{CO_2,MEA} &= He_{N_2O,MEA} \left(\frac{He_{CO_2,H_2O}}{He_{N_2O,H_2O}} \right) \\
 He_{N_2O,MEA} &= 2.448 \times 10^5 \exp\left(\frac{-1348}{T_L}\right) \\
 He_{CO_2,H_2O} &= 3.52 \times 10^6 \exp\left(-\frac{2113}{T_L}\right) \\
 He_{N_2O,H_2O} &= 8.449 \times 10^6 \exp\left(-\frac{2283}{T_L}\right)
 \end{aligned} \tag{S31}$$

Henry's constant (H_{CO_2} in Pa) using activity coefficient model

$$\begin{aligned}
 \ln\left(\frac{H_i}{\gamma_i^\infty}\right) &= \sum_s \ln\left(\frac{H_{is}}{\gamma_{is}^\infty}\right) \frac{x_s (V_{is'}^\infty)^{2/3}}{\sum_{s'} x_{s'} (V_{is'}^\infty)^{2/3}} \quad s = s' \in \{MEA, H_2O\} \\
 \ln H_{is} &= a_{is} + \frac{b_{is}}{T} + c_{is} \ln(T) + d_{is} T, \quad i = CO_2, \quad s = H_2O \\
 H_{is} &= 6.6434 \times 10^8 \exp\left(\frac{-896.5}{T}\right), \quad i = CO_2, \quad s = MEA
 \end{aligned} \tag{S32}$$

Table S7: solute -solvent pair parameters of Henry's constant

Component i	CO ₂
Component s	H ₂ O
Temperature units	K
a_{is}	170.7126
b_{is}	-8477.711
c_{is}	-21.95743
d_{is}	0.0057807

V_{is}^∞ is calculated from the Brelvi-O'Connell model

$$\begin{aligned}
 V_{is}^\infty &= \frac{1 - C_{is}}{\rho_s k_s}, \\
 C_{is} &= -\left(\frac{v_i}{v_s}\right)^{0.62} \exp(-2.4467 + 2.12074 \rho_s^r), \quad 2.0 \leq \rho_{s=\text{H}_2\text{O}}^r \leq 2.785 \\
 C_{is} &= -\left(\frac{v_i}{v_s}\right)^{0.62} \exp(3.02214 - 1.87085 \rho_s^r + 0.71955 (\rho_s^r)^2), \quad 2.785 \leq \rho_{s=\text{MEA}}^r \\
 k_s &= \exp\{\rho_s' [A + \rho_s' (B - C \rho_s')]\} - 1, \quad A = -0.42704, B = 2.089, C = 0.42367 \\
 \rho_s^r &= \rho_s v_s, \quad \rho_s' = \rho_s^r - 1 \\
 v_i &= v_{1,i}^{BO} + v_{2,i}^{BO}, \quad i = \text{CO}_2, \text{MEA}, \text{H}_2\text{O}
 \end{aligned} \tag{S33}$$

The Brelvi-O'Connell characteristic volume parameters are given in Table S8. ρ_s is the molar density in mol/cm³, hence the characteristic volume should be converted to similar units to compute the reduced density, ρ_s^r . The molar density of the pure solvent is obtained from the molar volume, V_s°

Table S8: Characteristic volume parameters (m³/kmol)

Species	$v_{1,i}^{BO}$	$v_{2,i}^{BO}$	Source
H ₂ O	0.0464	0.0	Brelvi et al. (1972)
MEA	0.225	0.0	Zhang et al. (2011)
CO ₂	0.177	-3.42e-4	Yan et al. (2010)

γ_i^∞ is the infinite dilution activity coefficient of molecular solute i in the mixed solvent. γ_{is}^∞ is the infinite dilution activity coefficient of molecular solute i in the pure solvent and x_s' is solute free mole fraction of the solvents.

Activity coefficient (NRTL model)

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}), \quad G_{ii} = 1$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}, \quad \tau_{ii} = 0$$
(S34)

Table S9: NRTL binary Parameters

Component i	H ₂ O	H ₂ O
Component j	MEA	CO ₂
a_{ij}	4.33838	0
a_{ji}	3.25515	69.38507
b_{ij}	-2197.53	0
b_{ji}	0	0
α_{ij}	0.3	0.3

Concentration-based Equilibrium constant

$$K_i \left(\text{m}^3/\text{kmol} \right) = \exp \left(a_i + \frac{b_i}{T_L} + c_i \ln T_L \right)$$
(S35)

Table S10: Equilibrium constants

constant	a_i	b_i	c_i
K_1	233.4	-3410	-36.8
K_2	176.72	-2909	-28.46

TRANSPORT PROPERTIES

Viscosity

Vapor phase

Pure component

Sutherland equation is used for CO₂, N₂ and O₂.

$$\mu_{v,i} \text{ (Pa.s)} = \frac{\mu_{v,i0}}{1000} \left(\frac{0.555T_{i0} + C_i^*}{0.555(T + 459.67) + C_i^*} \right) \left((T + 459.67) / T_{i0} \right)^{3/2} \quad (\text{S36})$$

Where T is temperature in kelvin.

Lucas method of corresponding states is used for water vapor(Reid et al. 1987).

Table S11:Sutherland's parameters

	$\mu_{v,i0}$	T_{i0}	C_i^*
CO ₂	0.01480	527.67	240
N ₂	0.01781	540.99	111
O ₂	0.02018	526.05	127

Viscosity of vapor mixture(Wilke 1950)

$$\mu_v \text{ (Pa.s)} = \sum_i \frac{\mu_{v,i}}{\left(1 + \frac{1}{y_i} \sum_{\substack{j=1 \\ j \neq i}}^{j=n} y_j \phi_{ij} \right)} \quad (\text{S37})$$

$$\phi_{ij} = \frac{\left[1 + (\mu_{i,v} / \mu_{j,v})^{1/2} (MW_j / MW_i)^{1/4} \right]^2}{(2\sqrt{2}) \left[1 + (MW_i / MW_j) \right]^{1/2}}$$

Liquid phase

$$\mu_L \text{ (Pa s)} = \frac{\mu_{H_2O}}{1000} \exp \left(\frac{\left[(a_\mu \Omega + b_\mu) T_L + c_\mu \Omega + d_\mu \right] \left[\alpha (e_\mu \Omega + f_\mu T + g_\mu) + 1 \right] \Omega}{T_L^2} \right)$$

$$\mu_{H_2O} \text{ (mPa s)} = 1.002 \times 10^{\frac{1.3272 \left[293.15 - T_L - 0.001053 (T_L - 293.15)^2 \right]}{T_L - 168.15}}$$

$$\Omega = 100r, \quad \text{where } r = \left[\frac{MW_{MEA} x_{MEA}}{MW_{MEA} x_{MEA} + MW_{H_2O} x_{H_2O}} \right]$$

$$\alpha \left(\frac{\text{mol CO}_2}{\text{mol MEA}} \right) = \frac{x_{CO_2}}{x_{MEA}}$$
(S38)

Table S12: Liquid viscosity parameters (Morgan et al. 2015)

a_μ	b_μ	c_μ	d_μ	e_μ	f_μ	g_μ
-0.0838	2.8817	33.651	1817	0.00847	0.0103	-2.3890

Surface Tension

Pure component

$$\sigma_i \text{ (N/m)} = c_{1,i}^\sigma \left(1 - \frac{T_L}{T_{c,i}} \right)^{c_{2,i}^\sigma + c_{3,i}^\sigma (T_L/T_{c,i}) + c_{4,i}^\sigma (T_L/T_{c,i})^2} \quad i \in \{\text{MEA, H}_2\text{O}\}$$

$$\sigma_{CO_2} \text{ (N/m)} = S_1 r^2 + S_2 r + S_3 + T (S_4 r^2 + S_5 r + S_6)$$
(S39)

Table S13:: Parameters for pure component surface tension

(Asprion 2005)	$c_{1,i}^\sigma$	$c_{2,i}^\sigma$	$c_{3,i}^\sigma$	$c_{4,i}^\sigma$	$T_{c,i}$ (K)	
MEA	0.09945	1.067	0	0	614.45	
H ₂ O	0.18548	2.717	-3.554	-2.047	647.13	
(Morgan et al. 2015)	S_1	S_2	S_3	S_4	S_5	S_6
CO ₂	-5.987	3.7699	-0.43164	0.018155	-0.01207	0.002119

Liquid solution

$$\begin{aligned}\sigma_L \text{ (N/m)} &= \sigma_{H_2O} + (\sigma_{CO_2} - \sigma_{H_2O}) F_{\sigma, CO_2} x_{CO_2} + (\sigma_{MEA} - \sigma_{H_2O}) F_{\sigma, MEA} x_{MEA} \\ F_{\sigma, CO_2} &= a_\sigma + b_\sigma \alpha + c_\sigma \alpha^2 + d_\sigma r + e_\sigma r^2 \\ F_{\sigma, MEA} &= f_\sigma + g_\sigma \alpha + h_\sigma \alpha^2 + i_\sigma r + j_\sigma r^2\end{aligned}\tag{S40}$$

Table S14: Surface tension parameters(Morgan et al. 2015)

a_σ	b_σ	c_σ	d_σ	e_σ
2.4558	-1.5311	3.4994	-5.6398	10.2109
f_σ	g_σ	h_σ	i_σ	j_σ
2.3122	4.5608	-2.3924	5.3324	-12.0494

Diffusivity

Vapor phase

$$D_{ij} \text{ (m}^2\text{/s)} = 1.013 \times 10^{-2} T_V^{1.75} \frac{\sqrt{(M_i + M_j)/M_i M_j}}{P(\sqrt[3]{V_{Di}} + \sqrt[3]{V_{Dj}})^2}\tag{S41}$$

Table S15: Diffusion Volumes in Fuller-Schettler-Giddings Correlation

MEA	H ₂ O	CO ₂	N ₂	O ₂
58.62	13.1	26.7	18.5	16.3

Effective or pseudo binary diffusivity (Wilke et al. 1955)

$$D_{V,i} \text{ (m}^2\text{/s)} = \frac{1 - y_i}{\sum_{\substack{j=1 \\ j \neq i}}^n \frac{y_j}{D_{ij}}}\tag{S42}$$

Liquid phase

CO₂

$$D_{L,CO_2} \text{ (m}^2\text{/s)} = (a_0 + a_1 C_{MEA,L} + a_2 C_{MEA,L}^2) \exp\left(\frac{b_0 + b_1 C_{MEA,L}}{T_L}\right) \quad (\text{S43})$$

Where $C_{MEA,L}$ is the concentration of MEA in the liquid and T is temperature in kelvin.

Table S16: Ying and Eimer (2012) diffusivity parameters for CO₂ in aqueous MEA mixture

Parameters	a_0	a_1	a_2	b_0	b_1
Values	2.35×10^{-6}	2.9837×10^{-8}	-9.7078×10^{-9}	-2119	-20.1320

MEA

(Snijder et al. 1993)

$$D_{L,MEA} \text{ (m}^2\text{/s)} = \exp\left(-13.275 - \frac{2198.3}{T_L} - 7.8142 \times 10^{-5} C_{MEA,L}\right) \quad (\text{S44})$$

MEACOO⁻

(Hoff et al. 2004)

$$D_{L,MEACOO^-} = \exp\left(-22.64 - \frac{1000}{T_L} - 0.7 \ln \mu_L\right) \quad (\text{S45})$$

CORRELATIONS FOR TRANSFER RATES, COLUMN HYDRAULICS AND KINETICS

Mass transfer coefficients

Chinen et al. (2018) have reported that the mass transfer correlations by Billet and Schultes (1999) and the interfacial area model of Tsai (2010) provide good estimates for MEA-CO₂-H₂O system. The values of C_V and C_L obtained from their integrated approach of simultaneously regressing the mass transfer and interfacial area model parameters are used in this work.

$$\begin{aligned}
 k_{V,i} \cdot a_e &= C_V \frac{1}{(\varepsilon_p - \varepsilon_L)^{1/2}} \frac{a^{3/2}}{d_h^{1/2}} D_{V,i} \left(\frac{u_V}{a v_V} \right)^{3/4} \left(\frac{\mu_V}{\rho_V D_{V,i}} \right)^{1/3} \left(\frac{a_e}{a} \right); \quad C_V = 0.35 \\
 k_{L,CO_2} \cdot a_e &= C_L \cdot 12^{1/6} \left(\frac{u_L}{\varepsilon_L} \right)^{1/2} \left(\frac{D_{L,CO_2}}{d_h} \right)^{1/2} a \left(\frac{a_e}{a} \right); \quad C_L = 0.203 \\
 d_h &= 4 \frac{\varepsilon_p}{a_p} \quad \varepsilon_p = 0.97; a_p = 250 \text{ m}^2 \text{m}^{-3}
 \end{aligned} \tag{S46}$$

Interfacial area model

The regressed interfacial area model of Tsai (2010) by Chinen et al. (2018)

$$\frac{a_e}{a_p} = 1.42 \left[\frac{\rho_L}{\sigma_L} g^{1/3} \left(\frac{u_L A}{L_p} \right)^{4/3} \right]^{0.12} \tag{S47}$$

Vapor phase heat transfer coefficient

The convective heat transfer coefficient in the vapor phase is calculated using the Chilton-Colburn analogy

$$h_{VL} = k_{V,CO_2} C_{p,V} \rho_V \left(\frac{\lambda_V}{C_{p,V} \rho_V D_{V,CO_2}} \right)^{2/3} \tag{S48}$$

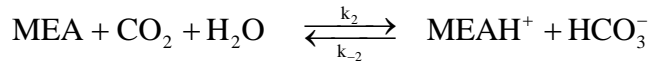
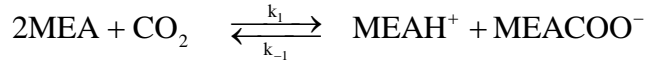
Second order rate constant

$$\begin{aligned}
 k_{rx} \text{ (m}^3 \text{/kmol} \cdot \text{s)} &= k_{\text{MEA}} C_{\text{MEA}} + k_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}} \\
 k_{\text{MEA}} \text{ (m}^6 \text{/kmol}^2 \cdot \text{s)} &= 2.003 \times 10^{10} \exp \left(-\frac{4742}{T_L} \right) \\
 k_{\text{H}_2\text{O}} \text{ (m}^6 \text{/kmol}^2 \cdot \text{s)} &= 4.147 \times 10^6 \exp \left(-\frac{3110}{T_L} \right)
 \end{aligned} \tag{S49}$$

Reconstitution of apparent species from true species

(Asprion 2004)

In the aqueous phase of the MEA-CO₂-H₂O system, the following no. of reactions(R=2) are considered,



STEP 1: order all species in a vector such that the apparent species appear first.

$$S = \left\{ \begin{matrix} s_1 & s_2 & s_3 & s_4 & s_5 & s_6 \\ \text{H}_2\text{O}, \text{CO}_2, \text{MEA}, \text{HCO}_3^-, \text{MEACOO}^-, \text{MEA}^+ \end{matrix} \right\}^T$$

Step 2: Create the matrix of stoichiometric coefficients of dimensions $R \times S$ using the ordering in step 1.

$$(v_{i,k}) = \begin{pmatrix} s_1 & s_2 & s_3 & s_4 & s_5 & s_6 \\ 0 & -1 & -2 & 0 & 1 & 1 \\ -1 & -1 & -1 & 1 & 0 & 1 \end{pmatrix} \begin{matrix} R_1 \\ R_2 \end{matrix}$$

Step 3: create two vectors of mole numbers $\bar{\mathbf{n}}$ and $\bar{\bar{\mathbf{n}}}$ such that, $\bar{\mathbf{n}}$ contains the first S-R elements as ordered in step 1 and $\bar{\bar{\mathbf{n}}}$ contains the remaining elements. Then, split the matrix, $(v_{i,k})$ accordingly into \bar{v} and $\bar{\bar{v}}$.

$$\bar{\mathbf{n}} = \begin{pmatrix} n_{\text{H}_2\text{O}} \\ n_{\text{CO}_2} \\ n_{\text{MEA}} \\ n_{\text{HCO}_3^-} \end{pmatrix}, \quad \bar{\bar{\mathbf{n}}} = \begin{pmatrix} n_{\text{MEACOO}^-} \\ n_{\text{MEA}^+} \end{pmatrix}, \quad \bar{v} = \begin{pmatrix} 0 & -1 & -2 & 0 \\ -1 & -1 & -1 & 1 \end{pmatrix}, \quad \bar{\bar{v}} = \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix}$$

Step 4: reconstitute the apparent species using initial no. of mols, $\bar{\mathbf{n}}^0$ defined as:

$$\bar{\mathbf{n}}^0 = \bar{\mathbf{n}} - \bar{v}^T (\bar{\bar{v}}^{-1})^T (\bar{\bar{\mathbf{n}}})$$

$$\bar{v}^T (\bar{\bar{v}}^{-1})^T = \begin{pmatrix} 1 & -1 \\ 0 & -1 \\ -1 & -1 \\ -1 & 1 \end{pmatrix} \Rightarrow \bar{v}^T (\bar{\bar{v}}^{-1})^T (\bar{\bar{\mathbf{n}}}) = \begin{pmatrix} n_{\text{MEACOO}^-} - n_{\text{MEA}^+} \\ -n_{\text{MEA}^+} \\ -n_{\text{MEACOO}^-} - n_{\text{MEA}^+} \\ -n_{\text{MEACOO}^-} + n_{\text{MEA}^+} \end{pmatrix}$$

$$\begin{aligned}
\bar{n}_{\text{H}_2\text{O}}^0 &= n_{\text{H}_2\text{O}} - n_{\text{MEACOO}^-} + n_{\text{MEA}^{\text{H}^+}} && \text{(H}_2\text{O balance)} \\
\bar{n}_{\text{CO}_2}^0 &= n_{\text{CO}_2} + n_{\text{MEA}^{\text{H}^+}} && \text{(CO}_2 \text{ balance)} \\
\bar{n}_{\text{MEA}}^0 &= n_{\text{MEA}} + n_{\text{MEACOO}^-} + n_{\text{MEA}^{\text{H}^+}} && \text{(MEA balance)} \\
\bar{n}_{\text{HCO}_3^-}^0 &= n_{\text{HCO}_3^-} + n_{\text{MEACOO}^-} - n_{\text{MEA}^{\text{H}^+}} && \text{(Charge balance)}
\end{aligned}
\Rightarrow
\boxed{
\begin{aligned}
\bar{n}_{\text{H}_2\text{O}}^0 &= n_{\text{H}_2\text{O}} - n_{\text{MEACOO}^-} + n_{\text{MEA}^{\text{H}^+}} \\
\bar{n}_{\text{CO}_2}^0 &= n_{\text{CO}_2} + n_{\text{HCO}_3^-} + n_{\text{MEACOO}^-} \\
\bar{n}_{\text{MEA}}^0 &= n_{\text{MEA}} + n_{\text{MEACOO}^-} + n_{\text{MEA}^{\text{H}^+}}
\end{aligned}
}$$

$\bar{n}_{\text{HCO}_3^-}^0 = 0$, initial number of moles of non-apparent species is zero .

Table S17 : Absorber flow streams -NCCC Steady-State data

CASES	1	2	3	4	5	6	7
Lean solvent absorber flowrate (kg/hr)	6804	11794	3175	6804	6804	11643	3175
Lean solvent absorber loading (mol CO ₂ /MEA)	0.145	0.247	0.083	0.108	0.347	0.154	0.239
Lean solvent MEA composition (g MEA/MEA+H ₂ O)	0.298	0.312	0.31	0.306	0.307	0.285	0.311
Lean solvent absorber inlet temperature (°C)	40.97	40.52	46.72	41.57	40.87	40.57	42.66
Rich solvent absorber flowrate (kg/hr)	7242	12284	3343	7212	7063	12043	3337
Rich solvent absorber loading (mol CO ₂ /MEA)	0.384	0.385	0.47	0.295	0.469	0.275	0.474
Rich solvent MEA composition (g MEA/MEA+ H ₂ O)	0.3	0.314	0.328	0.308	0.309	0.289	0.318
Flue gas flowrate (kg/hr)	2266	2261	2261	2253	2255	2255	2250
Flue gas CO ₂ weight fraction	0.1731	0.1718	0.1724	0.1395	0.1381	0.1393	0.1401
Flue gas H ₂ O weight fraction	0.0462	0.053	0.0525	0.0505	0.0464	0.0466	0.0533
Flue gas N ₂ weight fraction	0.7116	0.7066	0.7072	0.7152	0.7183	0.7193	0.7134
Flue gas O ₂ weight fraction	0.069	0.0686	0.0678	0.0948	0.0971	0.0948	0.0932
Flue gas inlet temperature (°C)	42.48	44.94	44.73	43.78	42.18	42.47	44.87
Absorber pressure (kPa)	108.82	107.06	107.65	106.94	107.1	107.26	107.49

Table S18 : Absorber intercoolers between the packed beds -NCCC Steady-State data

CASES	1	2	3	4	5	6	7
Intercooler 1 flowrate (kg/hr)	7364.83	12340.85	3848.86	7357.23	7539.09	11634.52	3832.25
Intercooler 1 return temperature (°C)	40.13	40.19	43.34	41.15	43.39	39.99	43.31
Intercooler 2 flowrate (kg/hr)	7421.57	12261.52	2429.55	7180.54	7179.52	11504.64	2335.07
Intercooler 2 return temperature (°C)	43.32	43.32	43.33	43.36	43.26	40.39	40.03
Number of absorber beds/ intercoolers	3/2	3/2	3/2	3/2	3/2	3/2	3/2

Table S19: Stripper, reboiler and heat exchanger (HX) NCCC steady state data

CASES	1	2	3	4	5	6	7
Stripper pressure (kPa)	183.87	182.06	184.15	183.43	179.88	183.45	182.84
Rich solvent stripper inlet temperature (°C)	104.8	104.8	97.6	109	95.7	110.1	98.4
Stripper solvent exit temperature (°C)	120.18	117.43	122.53	121.68	110.21	120.35	117.69
Reboiler duty (kW)	431	430	427	677	171	677	166
Lean solvent HX flowrate (kg/hr)	6811.2	11804.4	2998.8	6811.2	6811.2	3178.8	6811.2
Lean solvent HX temperature, inlet/exit (°C)	119.3/57.5	116.6/63.8	103.3/51.6	120.8/58.5	109.5/50.5	119.7/61.7	116.7/51.9
Rich solvent HX flowrate (kg/hr)	7246.8	12294.0	3344.4	7218.0	7070.4	3340.8	7246.8
Rich solvent HX temperature, inlet/exit (°C)	53.4/111.8	59.3/110.1	46.6/97.4	56.1/110.5	45.8/103.0	57.7/111.8	48.4/108.9

Table S20 : TCM absorber 2015 baseline data from Faramarzi et al. (2017).

Flue gas supply rate (Sm^3/h)		59430
Flue gas supply temperature ($^{\circ}\text{C}$)		29.8
Flue gas supply pressure (barg)		0.01
Flue gas supply CO_2 concentration (vol%)		3.7
Flue gas supply O_2 concentration (vol%)		14.6
Flue gas supply water content (vol%)		3.7
Lean amine supply flow rate (kg/h)		57434
Lean MEA concentration (wt%)		31
Lean CO_2 loading (mol CO_2 /mol MEA)		0.2
Active absorber packing height (m)		24
Lean amine supply temperature ($^{\circ}\text{C}$)		37
Absorber Beds	Height (m)	Temperature ($^{\circ}\text{C}$)
Upper Absorber Bed	23.5	47.4
	22.5	51.7
	21.5	51.6
	20.5	50.5
	19.5	49.9
	18.5	48.9
Middle Absorber Bed	17.5	47.2
	16.5	46.0
	15.5	44.4
	14.5	43.1
	13.5	42.2
	12.5	40.9
Lower Absorber Bed	11.5	40.6
	10.5	41.6
	9.5	37.4
	8.5	37.1
	7.5	35.9
	6.5	34.3
	5.5	34.1
	4.5	33.8
	3.5	32.9
	2.5	33.2
1.5	32.5	
0.5	32.4	

Table S21: TCM Stripper 2015 baseline data from Faramarzi et al. (2017).

Stripper overhead pressure (barg)		0.91
Stripping section packing height (m)		8
Rich solution supply temperature (°C)		110.7
Stripper Bed	Height (m)	Temperature (°C)
	7	102.7
	6	103.1
	5	104.5
Stripper Packing	4	107.7
	3	112.1
	2	114.7
	1	119.4
Stripper sump temperature (°C)		121.0

$$\text{Gas-side \% capture} = \frac{\text{flowrate}_{\text{CO}_2,\text{IN}}^{\text{absorber,gas}} - \text{flowrate}_{\text{CO}_2,\text{OUT}}^{\text{absorber,gas}}}{\text{flowrate}_{\text{CO}_2,\text{IN}}^{\text{absorber,gas}}} \times 100,$$

(S50)

$$\text{Liquid-side \% capture} = \frac{\text{flowrate}_{\text{CO}_2,\text{OUT}}^{\text{absorber,liquid}} - \text{flowrate}_{\text{CO}_2,\text{IN}}^{\text{absorber,liquid}}}{\text{flowrate}_{\text{CO}_2,\text{IN}}^{\text{absorber,gas}}} \times 100$$