

DYNAMIC MODEL FOR REMOVAL OF CARBON DIOXIDE FROM A POST COMBUSTION PROCESS WITH MONOETHANOLAMINE

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Abstract

A dynamic model for simulating a CO₂ capture system from post combustion gases is developed. The model consists of an absorber, a de-absorber, a re-boiler, a condenser, two heat exchangers and two pumps. More attention is given to the distribution models of the reactive absorber and the reactive de-absorber as they are considered to be the main components. The reactive absorber/de-absorber is discretized into a number of slices, while the mass transfer between the phases are modeled using the classical two-film theory approach in each stage. Multicomponent mass and heat transfer, and reaction kinetics are considered for the development of the model. A major effort is dedicated to defining the interface concentrations, diffusion fluxes, fluid properties and equilibrium constants.

The model is implemented in Matlab, and the effect of the number of slices on the computation time, geometry of the absorber and de-absorber, and accuracy of the model are analyzed. The equilibrium constants used for defining the reaction kinetics are validated with speciation diagrams. Certain perturbations are made to observe the model efficiency in various conditions. The model equations are solved using the method of lines (MOL).

1 Introduction

Capture and storage of carbon dioxide from post combustion gases produced by burning fossil fuels are an important operation in the global aim of reduction of CO₂ emissions. Up to 60% of CO₂ emissions are from fossil fuel point sources, mostly from coal, oil and natural gas fired power stations [10]. A variety of technologies are available for the removal of CO₂ from the post combustion gases among which are membrane separation, low temperature distillation, physical adsorption, chemical adsorption, physical absorption and chemical absorption [10]. The majority of CO₂ capture applications so far have been for the removal of CO₂ for gas cleaning purposes where most of the CO₂ is released back into the atmosphere. This paper describes a dynamic model of a post combustion CO₂ capture plant by chemical absorption in a monoethanolamine (MEA) solution and a subsequent de-absorption.

MEA is widely used for amine-absorption of CO₂ due to the fast reaction rates with CO₂ and the higher saturation pressure which minimizes evaporation losses [13]. The disadvantages of MEA are the high heat of reaction which is required to reverse the reaction with CO₂ [2], and high corrosiveness [21].

The plant model consists of an absorber, a de-absorber, a reboiler, a condenser, two heat exchangers and two pumps. The two heat exchangers are a process-process heat exchanger and a process-utility heat exchanger. Figure 1 gives a sketch of the CO₂ capture system which is considered in this work.

The paper is organized as follows. In section 2, the model development is described, in section 3, the simulation setup is given, in section 4, some results are discussed, and in section 5, some model perturbations are analyzed. Finally, conclusions are given together with possible future work.

2 Model Development

2.1 Absorption and De-absorption Tower Modelling

The dynamic model includes species and energy conservation equations for the absorption column and the de-absorption column. The model is based on two-film theory where the liquid phase is treated separately from the vapour phase. The connection between these two entities is made by introducing the interfacial area through which mass and energy exchange takes place. The size of the interfacial area depends on the packing type used in the absorption and de-absorption towers, in this case the Montz B 200 metal structured packing [3]. The towers are discretized into a number of slices along the height. Each slice is assumed to be a continuous stirred tank reactor.

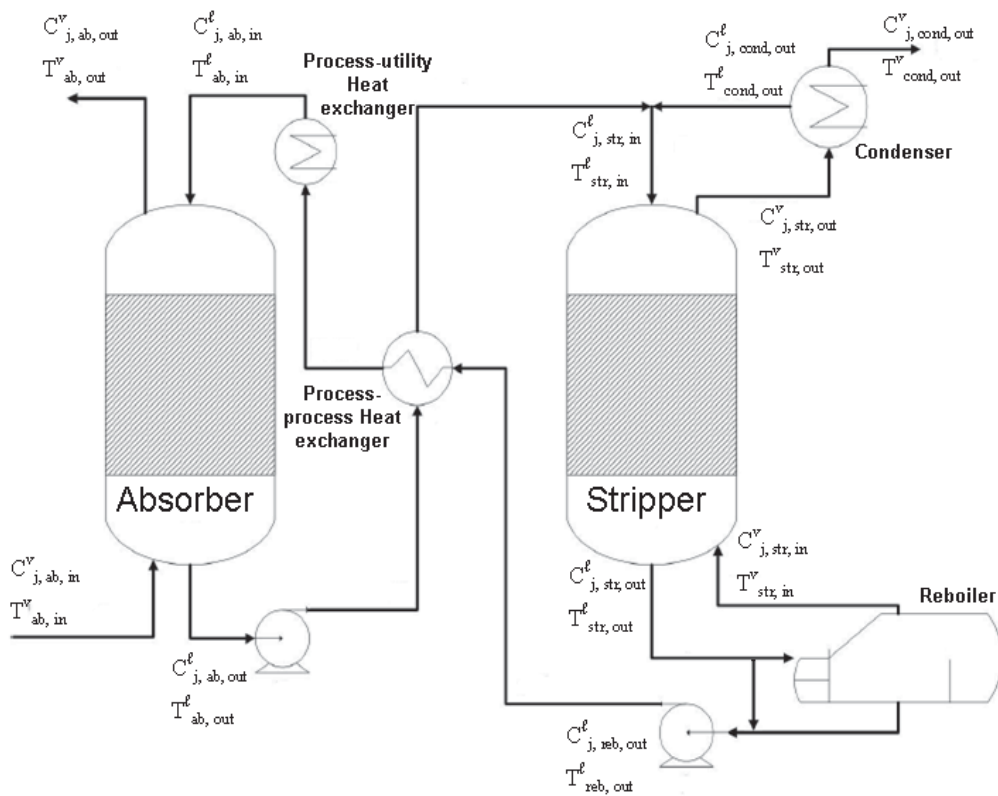


Figure 1: Flow sheet of the modelled post combustion CO₂ capture plant.

The velocities inside the towers could be modelled using momentum balance, which shows a variation of less than 0.05% [8]. Therefore the liquid and vapour velocities inside the absorption and de-absorption towers are assumed to be constant. The reactions in the vapour phase are considered to be insignificant. It is assumed that the system is well insulated. Mixing rules are applied assuming ideal solutions for both liquid and vapour phases. Specific enthalpies are assumed to be dependent on temperature only due to negligible pressure change within the tower.

The species and energy conservation equations of the liquid and vapour phases are presented by (1) to (4).

$$\frac{\partial c_j^\ell}{\partial t} = u^\ell \frac{\partial c_j^\ell}{\partial z} - \frac{1}{V} \cdot \dot{n}_{\text{trans},j} + r_j \quad (1)$$

$$\frac{\partial c_j^v}{\partial t} = -u^v \frac{\partial c_j^v}{\partial z} + \frac{1}{V} \cdot \dot{n}_{\text{trans},j} \quad (2)$$

$$\frac{\partial T^\ell}{\partial t} = u^\ell \frac{\partial T^\ell}{\partial z} - \frac{1}{V} \cdot \frac{\sum_{j=1}^s (\dot{n}_{\text{trans},j} \cdot \Delta \tilde{H}_j^{vl})}{\sum_{j=1}^s (c_j^\ell \cdot \tilde{c}_{p,j}^\ell)} + \frac{1}{V} \cdot \frac{\dot{n}_{\text{trans},\text{CO}_2} \cdot (-\Delta \tilde{H}_R)}{\sum_{j=1}^s (c_j^\ell \cdot \tilde{c}_{p,j}^\ell)} - \frac{U \cdot a \cdot (T^\ell - T^v)}{\sum_{j=1}^s (c_j^\ell \cdot \tilde{c}_{p,j}^\ell)} \quad (3)$$

$$\frac{\partial T^v}{\partial t} = -u^v \frac{\partial T^v}{\partial z} + \frac{U \cdot a \cdot (T^\ell - T^v)}{\sum_{j=1}^s (c_j^v \cdot \tilde{c}_{p,j}^v)} \quad (4)$$

The interfacial molar transfer of the species excluding CO₂ are modelled by the Whitman two-film theory [22] with the mass transfer flux described by (5) or (6) where the driving force is the difference between the interfacial and bulk phase concentrations.

$$\dot{n}_{\text{trans},j} = k_j^\ell \cdot a \cdot V \cdot (c_j^\ell - c_j^{\ell*}) \quad (5)$$

$$\dot{n}_{\text{trans},j} = k_j^v \cdot a \cdot V \cdot (c_j^v - c_j^{v*}) \quad (6)$$

The empirical formulas given by [4] are used to calculate the mass transfer coefficient values. The interfacial concentrations are modeled using (7),

$$y_j^* = K_j \cdot x_j^*, \quad (7)$$

assuming equilibrium between the liquid and the vapour phases at the interface. Based on the above assumption, the interfacial equilibrium constant K_j is calculated using the fugacity coefficients of each species at each phase. The fugacity coefficients are here calculated using the Peng-Robinson equation of state ([6]).

A special relation, (8), which is developed using (5), (6) and Henry's law in combination, is used to model the interfacial transfer of CO₂. The overall mass transfer coefficient k_{ov,CO_2} , given by (9), includes an enhancement factor which is there to take into account the effect of the reactions on the transfer of CO₂ between the phases. Due to fast reactions it is assumed that the enhancement factor equals the so-called Hatta number [9].

$$\dot{n}_{\text{trans},\text{CO}_2} = -k_{ov,\text{CO}_2} \cdot a \cdot V \cdot (P_{\text{CO}_2} - H_{\text{CO}_2} \cdot c_{\text{CO}_2}^\ell) \quad (8)$$

$$k_{ov,\text{CO}_2} = \frac{1}{\frac{H_{\text{CO}_2}}{E \cdot k_{\ell,\text{CO}_2}} + \frac{R \cdot T^v \cdot Z^v}{k_{v,\text{CO}_2}}} \quad (9)$$

Chemical absorption into the amine solution is effective as the absorbed CO₂ reacts with MEA to produce carbamate ions (MEACOO⁻) and protonated MEA ions (MEA⁺H). An important part of the model development is to include the chemical reactions that are occurring in the liquid phase. The reaction between MEA and CO₂ has exothermal character, and it behaves as a heat source. A total of 6 chemical reactions as presented in [14] are included in the model and are listed below,



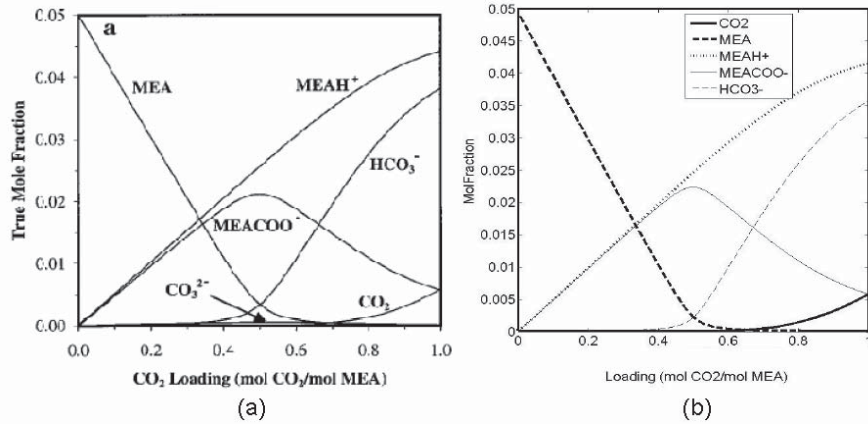


Figure 2: Species concentration diagrams at 313 K: (a) taken from [14], (b) developed in the work [19].

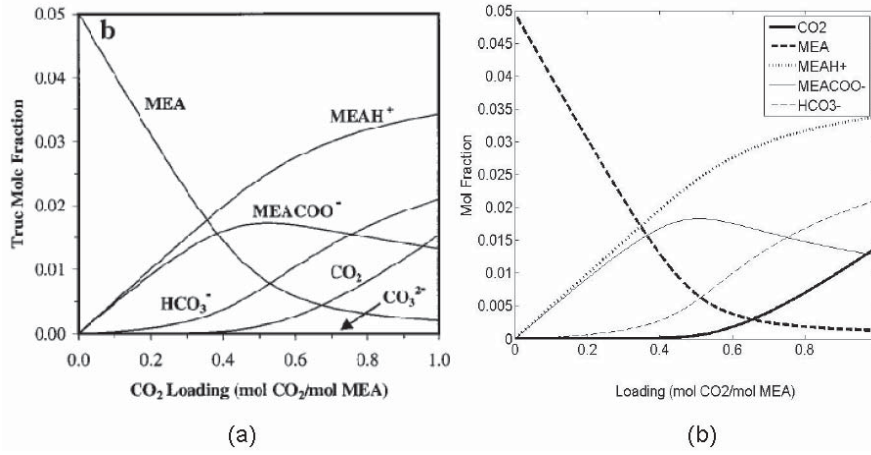


Figure 3: Species concentration diagrams at 373 K: (a) taken from [14], (b) developed in the work [19].

The molar generation term in the species conservation equation is developed using the reaction rates of the reactions (R1)–(R6). The forward reaction coefficients are given by [7], [11], [18] and the empirical representations of the equilibrium coefficients are given by [14]. The backward reaction coefficients are calculated using (10),

$$k_r = \frac{k_f}{K}. \quad (10)$$

The relations for equilibrium coefficients, which were developed with activity basis, are modified in order to use with concentration basis. The results are validated using speciation diagrams and are presented in the Figures 2 and 3.

The heat of generation of the reactions is calculated using a polynomial, which is found by fitting the data published by [13] on heat of reaction of CO₂ and MEA. The polynomials are given by (11) and (12) as a function of CO₂ loading (α),

$$\alpha < 0.55 : -\Delta\tilde{H}_R = (-2.798\alpha^5 + 1.6545\alpha^4 - 0.1686\alpha^3 - 0.04535\alpha^2 + 0.00839\alpha + 0.085017) \cdot 10^6 \quad (11)$$

$$\alpha \geq 0.55 : -\Delta\tilde{H}_R = (-0.1256\alpha^5 + 0.6377\alpha^4 - 1.2818\alpha^3 + 1.2757\alpha^2 - 0.6319\alpha + 0.129077) \cdot 10^7. \quad (12)$$

The pressures of the towers are not modeled and the pressure drop along the tower is given as a fixed value and linearly distributed along the tower. For a more accurate model, the pressure drop could be allowed for by use of pressure drop equation which considers packing properties [3].

| Input | Value | Units |
|--|-------|-------------------|
| CO ₂ molar flow into the system | 720 | mol/s |
| Absorber inlet gas temperature | 313 | K |
| Liquid volumetric flow from the absorber | 0.8 | m ³ /s |
| Reflux rate of the condenser | 10 | % |
| Reboiler pressure | 200 | kPa |
| Reboiler temperature | 394.2 | K |
| Liquid flow temperature to the absorber | 318 | K |
| Liquid temperature out of the condenser | 380 | K |
| Lean and rich pump head | 20 | m |

Table 1: Input values used in the model simulations.

2.2 Reboiler, Condenser and Heat Exchanger Modelling

A reboiler, a condenser and two heat exchangers are also considered for the modelling of the capture plant. The reboiler is modelled without using a flash calculation with a fixed reboiling rate of 10%, while the condenser is modelled with a simple material balance where a fixed reflux ratio is specified. The reboiler heat duty is calculated using (13),

$$\dot{Q}_{\text{reb}} = \sum_{j=1}^n \dot{n}_{\text{reb},j,\text{in}}^{\ell} \cdot \tilde{c}_{\text{p},j}^{\ell} \cdot (T_{\text{reb},\text{out}}^{\ell} - T_{\text{reb},\text{in}}^{\ell}) + \sum_{j=\text{H}_2\text{O}, \text{MEA}} \dot{n}_{\text{reb},j,\text{out}}^{\ell} \cdot \Delta \tilde{H}_j^{v\ell}. \quad (13)$$

An iterative procedure is used in order to estimate the liquid volume flow into the reboiler while keeping the outlet temperature constant. The condenser is modeled with a simple material balance and specified reflux rate. The heat exchangers are modeled using the relations given by (14) and (15),

$$\dot{Q}_{\text{hex}} = U \cdot A_{\text{hex}} \cdot \Delta T_{\text{LM}} \quad (14)$$

$$\dot{Q}_{\text{hex}} = \sum_{j=1}^n \dot{n}_{\text{rich},j}^{\ell} \cdot \tilde{c}_{\text{p},\text{rich},j}^{\ell} \cdot (T_{\text{rich},\text{out}}^{\ell} - T_{\text{rich},\text{in}}^{\ell}) = - \sum_{j=1}^n \dot{n}_{\text{lean},j}^{\ell} \cdot \tilde{c}_{\text{p},\text{lean},j}^{\ell} \cdot (T_{\text{lean},\text{out}}^{\ell} - T_{\text{lean},\text{in}}^{\ell}). \quad (15)$$

The minimum temperature difference between the streams in the process-process heat exchanger is kept as 10 K. An iterative procedure is applied for estimating the cold end exit temperature of the process-process heat exchanger. The process-utility heat exchanger removes the excess heat to get the required conditions at the absorber liquid inlet.

3 Model Simulation

The model is implemented in Matlab. The model for the tower is discretized in the spatial direction along the height using the method of lines. The `ode15s` solver is used to solve the complete model in the given time span. The system is characterized by the closed loop re-circulation of the MEA solution by introducing MEA and water make-up streams. The model is simulated assuming flue gas from a 400 MW natural gas fired power plant which produces 1,000,000 tons of CO₂ per year. The height of the towers and the number of discretized volumes used can be changed independently.

The input values used in this work are given in Table 1. Temperature dependency of the vapour phase viscosities are found by fitting the data from [16]. The correlation between the viscosity of the mixture and the concentrations of water, CO₂ and MEA is given by [8]. The specific heat capacity data of the species presented by [12] and [17] in the vapour and the liquid phases are approximated using the polynomial function. The thermal conductivity data are taken from [5]. The diffusivity of the gas is given by the Fuller equation given in [17]. The diffusivity of CO₂ in water is given in [20] and the N₂O analogy [1] is used to find the CO₂ diffusivity in the amine solution.

4 Results

A simulation of the model for 12 h of simulation time achieved approximately 57% removal efficiency (=amount of CO₂ removed / amount of CO₂ entered) in the absorber. To make the figures, towers were discretized into 10 slices for the simulation. The cost of CO₂ removal is estimated to be 4 MJ per kg of CO₂ removed. Figures 4 and 5 present the temperature profiles of the liquid phases in the de-absorption and absorption towers, respectively.

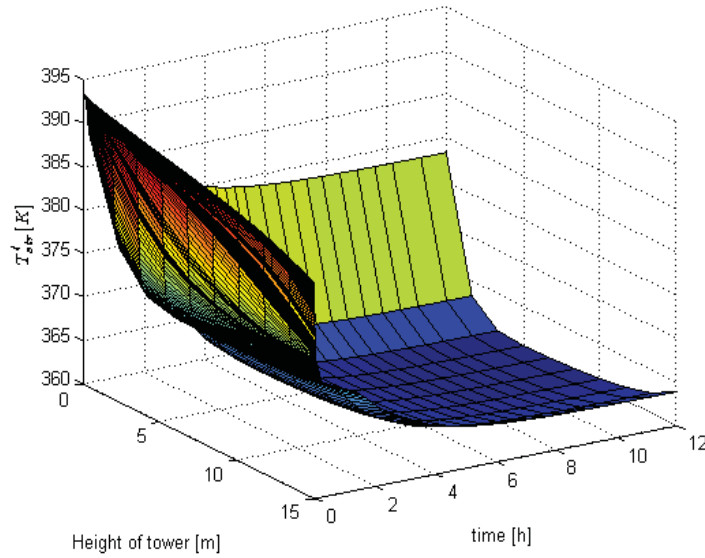


Figure 4: Temperature profile of the liquid phase in the de-absorption tower

| Alteration | Removal efficiency % | Removal cost (MJ/kg of CO ₂) |
|--------------------------|----------------------|--|
| <i>Reference case</i> | 57.0 | 4.2 |
| Absorber height 30 m | 57.9 | 4.1 |
| De-absorber height 10 m | 56.3 | 4.3 |
| Absorber diameter 30 m | 73.7 | 4.0 |
| Absorber diameter 20 m | 59.3 | 4.1 |
| De-absorber diameter 7 m | 54.3 | 4.1 |

Table 2: Perturbations

The temperature profile of the liquid phase in the de-absorption tower shows that after 12 h temperature distribution along the tower reaches steady state. This profile shows that the temperature in the de-absorption tower does not exceed the MEA degradation point (393.15 K, [15]). The temperature profile of the liquid phase of the absorption tower shows an initial increase due to the exothermal reactions followed by a gradual decrease due to the convective heat transfer with the gas phase.

The concentration profile of CO₂ in the gas phase of the absorption tower is presented in Figure 6. This shows that the concentration of CO₂ is being reduced as the gas stream flows towards the gas stack throughout the tower.

The concentration profile of MEA in the liquid stream of the de-absorption tower is presented in Figure 7. The concentration of MEA is increasing as the liquid stream flows towards the bottom of the tower due to regeneration.

5 Perturbations

Perturbations are done in comparison to a *reference case* which has the following specifications: absorber height = 25 m, de-absorber height = 15 m, absorber diameter = 16 m, de-absorber diameter = 5 m, absorber liquid volume flow out = 0.8 m³/s, number of slices = 5.

Increased height of the absorption tower gave an increase in the CO₂ removal efficiency while decreasing the required energy. The disadvantage with this case is the increase of the capital cost with the increased tower height. Decreased height of the de-absorber reduces the CO₂ removal efficiency with increased energy requirement. Increased diameter of the absorber results in reduced velocity of liquid and gas phases giving an increased retention time, which increases the efficiency and reduces the removal cost. By increasing the absorber diameter, the area available for the mass transfer increases and accordingly the removal efficiency increases. However, because of the larger diameter, the capital cost will be higher. Results showed that the CO₂ removal efficiency is increasing and the energy requirement is decreasing when the retention time is increased. Increased diameter of the de-absorber did not increase the removal efficiency, but it did slightly reduce the removal cost. The

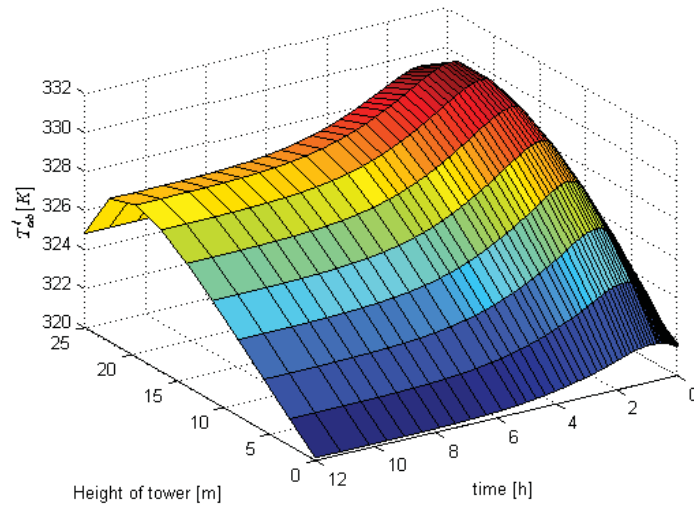


Figure 5: Temperature profile of the liquid phase in the absorption tower

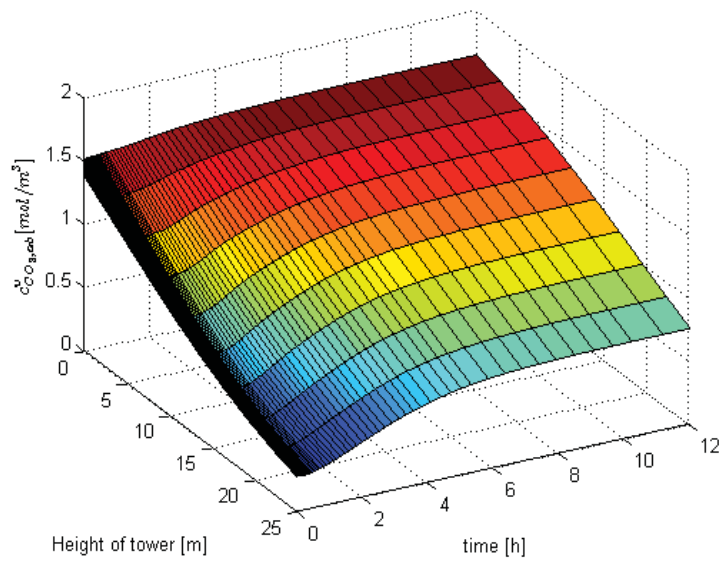


Figure 6: Concentration profile of CO_2 in the gas phase of the absorption tower

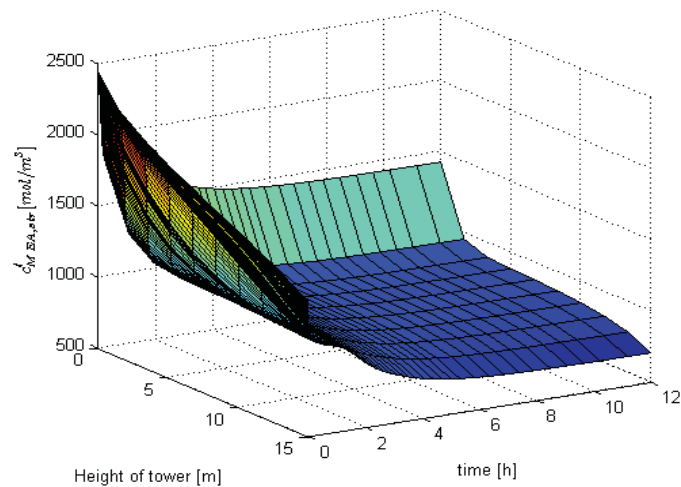


Figure 7: Concentration profile of MEA in the liquid phase of the de-absorption tower

reason is that the reduced velocity and the increased transfer area of the de-absorber play important roles in the purity of CO_2 coming out of the de-absorber, but not in the overall efficiency which is estimated based on absorber I/O streams.

6 Conclusions and future work

The absorption tower and the de-absorption tower are modelled using a rate based model approach. The common practice is to use equilibrium modelling for the de-absorption tower due to the high temperature conditions. However in the present work the same model is used for both absorption tower and the de-absorption tower. The results show that it is possible to model both towers using the rate based model which saved some model development time.

The interfacial molar transfer is modelled using the Whitman two-film theory, which uses Fick's law of diffusion. This approach, even though it is simpler than the state of the art Maxwell-Stefan approach, gave satisfying accuracy regarding the mass diffusion term. Simulations gave reasonable results and confirmed the tendencies of the concentrations and temperatures.

The present model can be improved by introducing more realistic models of the additional equipment such as the reboiler, the condenser, and heat exchangers. The CO_2 transfer in the boundary layer can be modelled more realistically without using the enhancement factor. The reboiler can be modelled with the steam flow as the control input rather than the outlet temperature. Interfacial molar transfer can be modelled with higher accuracy using the Maxwell-Stefan approach.

The model is intended for use in design considerations, but also for online control. Before the model is used for design and control, it should be validated against experimental data.

Nomenclature

| Main symbols | | | |
|--------------|--|---------|------------------------------|
| A | Area | r | Rate of generation |
| a | Specific area | s | Number of species |
| c | Concentration | T | Temperature |
| \tilde{c} | Molar heat capacity | t | Time |
| E | Enhancement factor | U | Overall heat transfer number |
| H | Henry's law constant | u | Velocity |
| \tilde{H} | Molar enthalpy | V | Volume of a slice |
| k | Mass transfer/reaction coefficient | x | Liquid phase molar fraction |
| K | Interfacial/reaction equilibrium coefficient | y | Vapour phase molar fraction |
| \dot{n} | Molar flow | Z | Compressibility factor |
| P | Pressure | z | Height |
| R | Universal gas constant | | |
| Subscripts | | | |
| con | Condenser | p | Constant pressure |
| f | Forward | R | Reactions |
| hex | Heat exchanger | r | Reverse |
| j | Number of species | reb | Reboiler |
| LM | Log mean temperature | trans | Interfacial transfer |
| ov | Overall | | |
| Superscripts | | | |
| ℓ | Liquid phase | $v\ell$ | Vapourization |
| s | Number of species | * | Interfacial value |
| v | Vapour phase | | |

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