A dynamic model for the de-absorption of carbon dioxide from Monoethanolamine solution

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Abstract

Due to the adverse effect of CO_2 from fossil fuel combustion on the earth's ecosystems, the most cost effective method for CO_2 capture is an important area of research. The predominant process for CO_2 capture currently employed by industry is chemical absorption in amine solutions. A dynamic model for the de-absorption process was developed with Monoethanolamine solution. Henry's law was used for modeling the vapour phase equilibrium of the CO_2, and fugacity ratios calculated by the Peng Robinson EOS were used for H_2O, MEA, N_2 and O_2. Chemical reactions between CO_2 and MEA were included in the model along with the enhancement factor for chemical absorption. Liquid and vapor energy balances were developed to calculate the liquid and vapour temperature, respectively. The model results compare favourably with other published results.

Keywords:
CO_2 de-absorption, dynamic model, amine

1 Introduction

The effect of carbon dioxide on the enhanced greenhouse effect is an important worldwide issue, with increasing research and emphasis to find the most cost effective method to capture CO_2 emissions from fossil fuel combustion. Approximately 60% of CO_2 produced is from point sources, with CO_2 fractions up to 14% for coal fired power stations and 8% for natural gas fired power stations [13].

The separation of the CO_2 into a pure stream (>95%) can be achieved by a variety of techniques, including membrane separation, low temperature distillation, adsorption and absorption [13]. The absorption of CO_2 into Monoethanolamine (MEA) by chemical absorption is presently the mostly favored method for the capture of carbon dioxide from fossil fuel combustion. A benefit of chemical absorption into amine solution is that at higher temperatures the chemical reaction can be reversed and the MEA recycled.

The majority of previous work on amine CO_2 capture is related to absorption models or on small scale experimental de-absorption. Hansen [7] developed a dynamic model for the absorption of CO_2 in MEA while Hoff [8] developed an absorption model with MEA and MDEA in a membrane contactor. Jamal et al [9] published work on absorption and desorption for small scale laboratory experiments, and Liu *et al.* [10] developed a full scale absorption and desorption model utilizing Aspen HYSYS. Bedelbayev [2] developed an absorption model implemented in Matlab for studying controllability issues, while Greer [6] developed a full scale model which was implemented in Matlab.

This paper presents the development of a dynamic model for the simulation of the de-absorption process. The first part of the paper describes the full scale process and the associated componeents. The dynamic model is developed in section 3 from the principles of diffusion from vapour to liquid taking into account the chemical reactions between the MEA and CO_2. The model validation and full scale simulation are included in section 4 and discussion and conclusions are in section 5.

2 Process description

Amine compounds react with CO_2 to form stable ionic compounds with the reaction reversing at higher temperatures.

A typical schematic of the de-absorption process is shown in fig. 1 where the main item of equipment is a stripping tower filled with packing material with a high surface to volume ratio (typically 200 m^2/m^3).

For the de-absorption process a rich stream (S1) of MEA and CO_2 from an absorption tower is pumped to the top of the stripping tower where it flows down
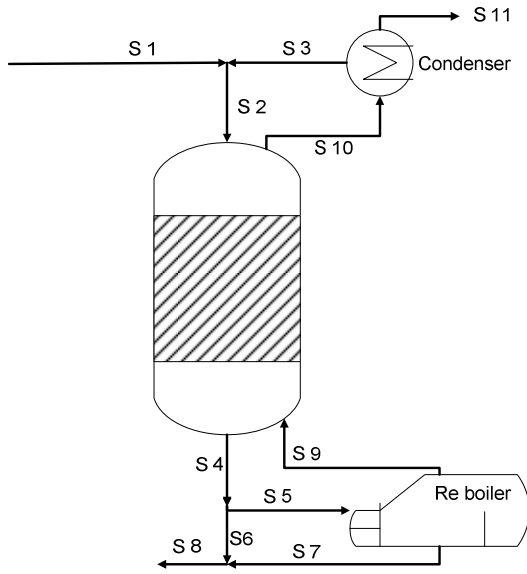
Fig. 1 Process flow diagram of de-absorption tower.

over the packing within the de-absorption tower. Stripping steam from the reboiler (S9) enters the tower at the bottom and flows up the tower in a counter current flow arrangement. As the rich liquid flows down the tower, the chemical reactions act in the reverse reaction and release the bound CO_2 from ionic form into the aqueous solution which then diffuses into the gas phase. The lean MEA solution exits at the bottom of the de-absorption tower and is returned to the absorption process (S8). A percentage of the lean mixture is directed to the reboiler to provide the stripping steam for the process (S5). The condenser cools the outgoing gas, and thus reduces the H_2O content and up-concentrates the amount of CO_2. Typically, the captured CO_2 requires more post processing such as dehydration and compression; this post processing is not discussed further here.

3 Model development

The mass transfer flux of each specie is a function of the driving force between the concentration in the bulk vapour and liquid phases as shown in fig. 2.
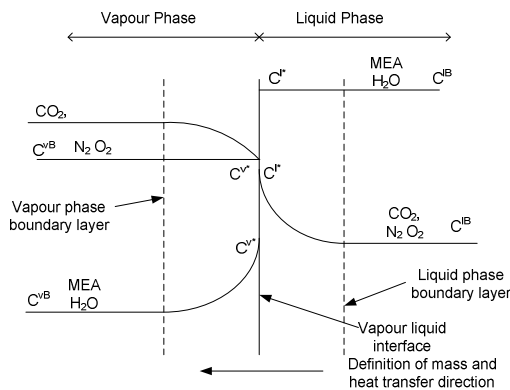

Fig. 2 Interphase concentration profile.

The general form of the transfer flux equation is shown in equation 1

$$\dot{n}_d = k_{la}a_w\left(C_i^* - C_i^B\right) \quad (1)$$

Here, $\dot{n}_d$ is the molar diffusion rate, k_{la} is the transfer coefficient, a_w is the interphase surface area, C_i^* is the interphase molar concentration of specie i in vapour liquid equilibrium, while C_i^B is the bulk concentration of specie i.

It is assumed for the H_2O and MEA that the concentration at the liquid side of the vapour-liquid interface is the same as the bulk liquid concentration. For the N_2 and the O_2 it is assumed that the concentration at the vapour side of the vapour-liquid interface is the same as the bulk vapour phase concentration. The fugacities of the species at the vapour liquid boundary were calculated and used to evaluate the concentration at the interface. At the interface it is assumed that there is phase equilibrium, therefore the fugacities of the liquid and vapour of each species are equal. Equation 2 relates the mol fraction in the vapour phase to that in the liquid phase by the ratio of the specie fugacity

$$y_i = Kx_i = \frac{\widehat{\varphi}_i^l}{\widehat{\varphi}_i^v}x_i \quad (2)$$

Being states, we know the liquid bulk phase concentration for the MEA and H_2O and the vapour bulk phase concentration for the N_2 and O_2. Then the mol fractions at the interface can be found by iteration and then the interface concentrations can be calculated. Equation 1 has the concentration difference as the driving force and an equivalent transfer area which is related to the surface area of the packing. The mass transfer coefficient is taken from an empirical formula derived by Billet [3] which is a function of the packing properties. The surface area available for transfer is a function of the specific surface area of the packing used and the wetted area of the packing. The formula for the wetted surface area is taken from Billet [4].

Henry's law is applied to relate the concentration of CO_2 in the bulk liquid phase to the bulk vapour phase concentration. By applying Henry's law, the interface concentration can be eliminated and a relationship between the bulk vapour and liquids applied. The resistance to mass transfer in the liquid and vapour phases is provided by the same formulas from Billet [3] as used for the other species and it is assumed there is resistance to mass transfer in the liquid and vapour phases. Henry's law is shown in equation 3

$$\dot{n}_d = \frac{1}{\frac{H_{CO_2}}{Ek_{la}^l a_w} + \frac{RT^v z^v}{k_{la}^v a_w}}\left(P_{CO_2}^v - H_{CO_2}C_{CO_2}^l\right) \quad (3)$$

The enhancement factor accounts for the continual removal of the CO_2 from the liquid film boundary layer by the chemical reaction of CO_2 with MEA.

The main reaction for the system is

$$CO_2 + MEA \leftrightarrow MEACOO^- + MEAH^+. \text{ (R1)}$$
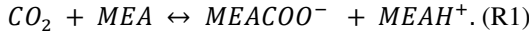
The forward reaction has a rate as in equation 4 and the reverse reaction has a rate as in equation 5.

$$r_f = k_f[MEA][CO_2] \quad \frac{mol}{s\,m^3} \quad where$$

$$k_f = 3.95x10^{10}\, exp\left(-\frac{6864}{T^l}\right) \quad \frac{m^3}{mol\,s} \quad (4)$$

$$r_r = k_r[MEAH^+][MEACOO^-] \quad \frac{mol}{s\,m^3}$$

$$where \quad k_r = \frac{K_e}{k_f} \quad (5)$$

The equilibrium constants are taken from Liu *et al.* [10] and the enhancement factor is shown in equation 6 and is the ratio of the mass transfer for a reacting and an un-reacting system i.e. what the mass transfer would be if the CO_2 did not react with the MEA in the film boundary layer. The enhancement factor is the Hatta number for this system and is taken from Perry [12].

$$E = \frac{\sqrt{D_{CO_2}k_f C_{MEA}^l}}{k_{la}^l} . \quad (6)$$

The energy balance is developed to provide the temperature model for the liquid and vapour phases. In the liquid phase the de-absorption reaction is endothermic and thus requires heat to proceed. The heat of reaction is the heat required for one mol of CO_2 to react with two moles of MEA and is 65000 J/mol CO_2 (ΔH_{RE}) [5]. There are also terms in the temperature equation for the spatial movement of the fluid, the sensible heat transfer and the diffusion heat transfer. It is assumed that the diffusion heat transfer is for MEA and H_2O only and that the liquid changes into a vapour within a control volume at the VLE interface. The sensible heat transfer is modelled by Newton's law of cooling as shown in equation 7 where the heat transfer coefficient is found using the Chilton-Colburn analogy relating the mass transfer coefficient to the heat transfer coefficient.

$$Q_s = U_T(T^l - T^v) \quad (7)$$

For the diffusion mass transfer, it is assumed that the vapourization of the liquid takes place in the liquid phase, hence it is already a vapour when it enters the vapour phase. Therefore the only terms in the temperature balance for the vapour phase are the spatial movement term and the sensible heat transfer

which is equal but opposite of the sensible heat term from the liquid phase.
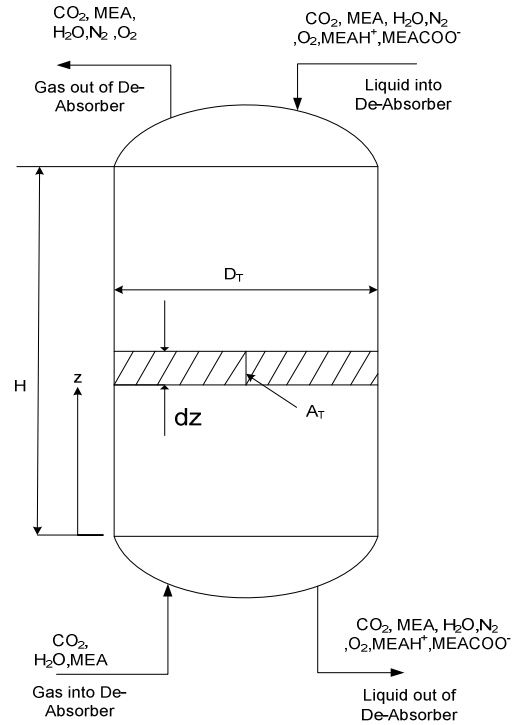

Fig. 3 PDE development of column.

The de-absorption column is modelled as a plug flow reactor with PDE's describing the species concentrations and the temperature in each phase. A schematic of the stripping tower is shown in figure 3 and a summary of the equations is shown below and in Tab. 1.

$$\frac{\partial c_i^l}{\partial t} = u\frac{\partial c_i^l}{\partial z} - \dot{n}_d + \dot{n}_g$$

$$\frac{\partial c_i^v}{\partial t} = -u\frac{\partial c_i^v}{\partial z} + \dot{n}_d$$

$$\frac{\partial T^l}{\partial t} = -u\frac{\partial T^l}{\partial z} - \frac{\dot{n}_d^T \Delta \tilde{H}^{vl}}{\left(C^l\right)^T \tilde{C}_p^l} - \frac{\dot{n}_{d,CO_2}\Delta H_{RE}}{\left(C^l\right)^T \tilde{C}_p^l} - \frac{U_T\left(T^l - T^v\right)}{\left(C^l\right)^T \tilde{C}_p^l}$$

$$\frac{\partial T^v}{\partial t} = -u\frac{\partial T^v}{\partial z} + \frac{U_T\left(T^l - T^v\right)}{\left(C^v\right)^T \tilde{C}_p^v}$$

Tab. 1 Species modelled by PDE.

Species	Gas phase	Liquid phase	Generation term	Diffusion term
CO_2	Yes	Yes	Yes	Yes
MEA	Yes	Yes	Yes	Yes
H_2O	Yes	Yes	No	Yes
N_2	Yes	Yes	No	Yes
O_2	Yes	Yes	No	Yes
$MEAH^+$	No	Yes	Yes	No
$MEACO^-$	No	Yes	Yes	No

At the bottom of the de-absorption tower, some of the liquid is transferred to a reboiler where the liquid is vaporised into stripping steam. The reboiler is modelled as a flash calculation with the inputs being the flash pressure, temperature and the percentage of the liquid flow fed into the reboiler. The reboiler consumes the largest amount of energy as heat is required to vapourize the liquid and provides the energy to reverse the chemical reactions. Typically the reboiler is heated by steam and has a maximum temperature of approximately 120 °C as this is the temperature at which the MEA will start to degrade.

The reactions in the de-absorption tower are reversed with increasing temperature so the higher the temperature the larger the amount of CO_2 released. A typical operating regime has a MEA concentration of up to 30% by weight. The greater the percentage of MEA, the less energy is consumed because if the MEA is 30% and the water is 70% then energy is required to heat up the 70% water for no benefit. Therefore it is advantageous to increase the MEA concentration and minimise the water concentration, but this has a trade off as above 30% MEA is highly corrosive and requires corrosion inhibitors and specialised equipment [10].

At the top of the de-absorption tower is a condenser which cools the vapour phase exiting the de-absorption column. The vapour is cooled to a designated temperature and a proportion of the vapour condenses into the liquid phase and is returned back to the de-absorption column. The temperature of the cooled liquid and the percentage refluxed back into the column are input variables in the model.

4 Simulation

4.1 Model validation

Model validation is performed by carrying out a simulation of the partial pressure of CO_2 versus CO_2 loading. CO_2 loading is the ratio of the CO_2 in free and ionic form (CO_2 aq and $MEACOO^-$) and the total MEA of the mixture. A plot of the simulation at a temperature of 400K is shown in figure 4. Various references include other reactions than that of reaction R1 in the process, most notably the formation of bicarbonate (HCO_3^-) and the reversion of the MEACOO- [10],[8]. A plot of the chemical species with the extra reactions is shown in figure 4. The operating range of the de-absorption process is an input loading of 0.45 of solution into the top of the tower where the CO_2 is subsequently stripped, and an output loading of 0.20. The dominant reaction for the typical loading is R1 where one mol of CO_2 reacts with 2 mols of MEA. At this loading the reversion of $MEACOO^-$ into MEA and HCO_3^- is not as signifiant as at higher CO_2 loadings, as indicated in figure 4. CO_2 reacts with H_2O to form bicarbonate but this reaction is typically slow and can typically be ignored for the de-absorption process [11]. Since the $MEAH^+$ and $MEACOO^-$ lines are so close in the operating

range, as shown in figure 4, it is justifired to run the simulation with only one dominant reaction.
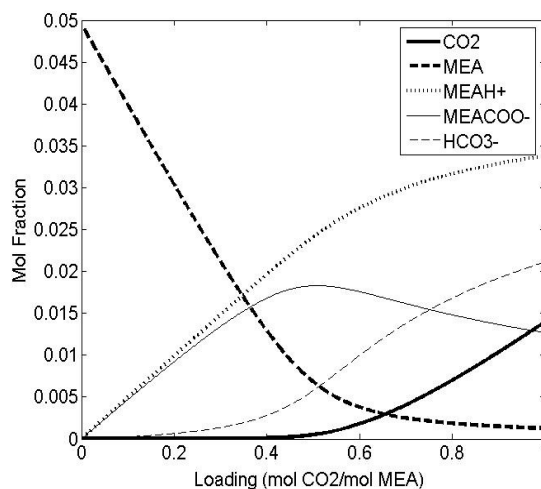

Fig. 4 Chemical species as a function of CO_2 loading at 400K.

4.2 Full simulation

The simulation is performed in Matlab from The MathWorks using the method of lines and ODE solver ode15s to solve the PDE. In total 14 PDE equations where solved simultaneously (liquid and gas phase for CO_2, MEA, H_2O, N_2 and O_2, liquid phase for $MEAH^+$ and $MEACOO^-$ and the temperature in the gas and liquid phase).

The inlet values are for a typical 400 MW natural gas power station producing 1 million tonnes of CO_2 per annum. The input values used in the model are displayed in Tab. 2.

Tab.2 Input values for model simulation.

Input	Value	Unit
Stripper Height	15	m
Stripper Diameter	6	m
Liquid flow rate	0.5	m^3/s
Liquid inlet temperature	383	K
Reboiler temperature	400	K
Reboiler flow (Stream S5)	3.5	%
Packing surface area	200	m^2/m^3
Tower Pressure	2	bar
$MEACOO^-$ (Liq)	2300	mol/m^3
$MEAH^+$ (Liq)	2300	mol/m^3
MEA (Liq)	400	mol/m^3
O_2 (Liq)	10^{-3}	mol/m^3
N_2 (Liq)	10^{-3}	mol/m^3
CO_2 (Liq)	10^{-1}	mol/m^3
H_2O (Liq)	38000	mol/m^3

Plots of the CO_2 concentration in the gas phase, the MEA concentration in the liquid phase, and liquid temperature are shown in figures 5, 6 and 7, respectively.
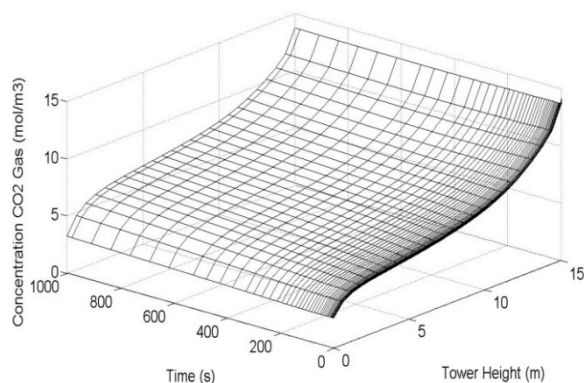
Fig. 5 Concentration of CO_2 in the gas phase.
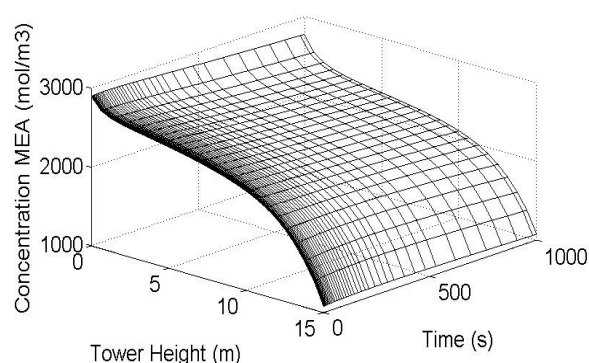

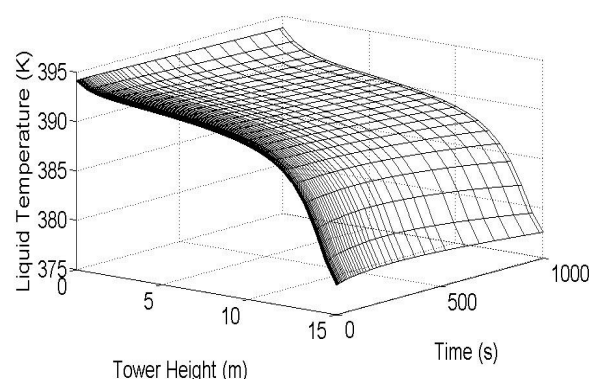
Fig. 6 Concentration of MEA in the liquid phase.

Fig. 7 Liquid temperature (K).

5 Discussion and conclusions

The modelling of the de-absorption process is a complex process as the system is a stiff system; the reactions have a time scale of milli-seconds, there is a slower process of diffusion and temperature change, and the even slower spatial movement of the fluids within the tower which has a retention time in the order of hours. Furthermore, the reaction rates as well as diffusion and fluid properties are all strong functions of the temperature: effort has been made to provide all variables as a function of temperature including density, diffusivity, viscosity, heat capacity, thermal conductivity, Henry's constants, chemical reaction rates, and equilibrium constants. The dominant reaction is the reaction of one mol of CO_2 with two moles of MEA forming $MEACOO^-$ and $MEAH^+$ which is reversed at elevated temperature.

The mass transfer of CO_2 is strongly dependant on the equilibrium constant for the chemical reaction. The equilibrium value dictates the ratio of the free aqueous CO_2 to the bound CO_2 in $MEACOO^-$. As the temperature increases, the ratio of free CO_2 increases in the liquid phase. The solubility of CO_2 in the liquid is also a function of temperature and decreases with elevated temperature, therefore the CO_2 diffuses faster into the gas phase. The ratio of the CO_2 in the liquid to vapour phase is given by Henry's constant. Henry's constant is a function of the temperature and the ionic strength of the mixture. A larger value for Henry's constant equates to a larger concentration of CO_2 in the vapour phase.

For the simulation, an inlet loading of 0.46 was used where the majority of the MEA was in the form of $MEAH^+$ and $MEACOO^-$. An outlet loading of 0.27 was achieved with a reboiler reflux of 30% and reboiler temperature of 400K. This required an energy consumption of 4.25 MJ per kg of CO_2 removed, which is in line with other literature sources [10],[14]. Figure 6 displays how the MEA concentration increases down the column as the reaction is reversed, releasing the bound MEA and CO_2. The temperature of the reboiler of 400 K enters the stripper at the bottom and decreases to 377K over the length of the de-absorption tower as the heat from the steam is transferred to heating up the liquid solution and reversing the chemical reaction. This is displayed in figure 7.

The species H_2O, MEA, N_2 and O_2 were modelled using the fugacity ratio between the liquid and vapour phase. The Peng Robinson EOS was used but the results where dependant of the interaction parameters and mixing rule used in solving the EOS. The accuracy of the liquid phase fugacity from the Peng Robinson EOS is unknown, but the overall results are similar to other estimates. The presence of O_2 and N_2 in the stripping process is low as the solubility of the N_2 and O_2 in the solution is low, therefore the inlet concentration in the liquid is minimal and the composition of the captured CO_2 is predominantly CO_2 and H_2O.

The overall control philosophy for the de-absorption process is linked to the absorption process [14]. The removal of CO_2 at minimal cost is the primary objective of the process and this is achieved by maximising the loading into the stripper and minimising the loading out. The loading out is reduced by adding stripping energy in the form of steam from the reboiler. The control of the stripping steam is achieved by manipulating the reboiler temperature and the amount of liquid refluxed to the reboiler

The simulation input does not represent the optimal solution, but provides a workable solution. For more robust optimisation, the absorption process and capital expenditure costs should be considered.

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