

NEQ Rate Based Modeling of an Absorption Column for Post Combustion CO₂ Capturing

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Abstract

Post combustion CO₂ capture via absorption into aqueous alkanolamine systems is considered to be the most mature and potential technique for CO₂ removal from the power plants' exhaust gases. Modeling and simulation of such plants have achieved an interesting place in research, and several steady state models already exist. Though steady state models are capable of giving an understanding of the process, dynamic models are most useful for controlling and optimizing the plants. A dynamic model for the absorption column in a CO₂ removal plant is been developed. Usability of simple thermodynamics for modeling is checked with the development of this model, instead of using complex thermodynamic models which are very popular in recent research. It is concluded that the steady state simulation results show a good agreement with the trend of the available pilot plant data. Dynamic predictions of the model indicate that the model is capable of handling an excitation of the inputs and reaches steady states. Yet, the whole CO₂ absorption plant has to be included into the dynamic model before it is ready to be used for control or optimization applications.

Keywords: CO₂ capture; Dynamic modelling; Absorption

1. Introduction

In spite of the research taking place in the field of CO₂ emission reduction, a sound solution for the capture procedure remains still as a challenge. The major portion of CO₂ emissions are claimed to be a result of power generation. There are three main techniques for CO₂ capturing that is suitable to be used in the power generation sector. Those are post-combustion capture, pre-combustion capture and oxy-fuel combustion [1]. Recent development and use of combined power cycles in the power generation sector although having impressive levels of performance and efficiency, their increased use has raised the importance of removal of CO₂ from the flue gases effectively. CO₂ capture by amine absorption and stripping is currently considered to be the most feasible option for the removal of carbon dioxide from the power plants' exhaust gases [2]. Monoethanolamine (MEA) is known to be the most widely used solvent for this.

Modeling work for such plants has mainly been done with the interest of process analysis and process optimization. Lars Øi has discussed some of the challenges in modeling of CO₂ removal by absorption [3].

Extensive usage of two modeling approaches, namely, the equilibrium stage modeling (EQ, the liquid and vapor phases are assumed to be in equilibrium) and non-equilibrium stage modeling (NEQ, the finite mass transfer rates across the liquid-vapor interface is considered) are found. The EQ stage approach is not very accurate because in actual operation, columns rarely, if ever, operate at equilibrium. Furthermore, modeling work has fallen into two

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categories: steady state modeling and dynamic modeling depending on the interests of the researchers. A dynamic simulator enables to study the transient behaviors of the total process, and the effect of integrated parts of the process [4].

In the present work a dynamic model is developed for an absorption tower of an MEA based CO₂ capture plant from the flue gas, following the NEQ approach. Some steady state results and dynamic predictions are produced. The results are compared with some experimental data found in the literature.

2. Model Development

A dynamic model for an absorber of a CO₂ capturing system is developed and implemented in MATLAB. The column is discretized along the height and a set of time dependant equations are developed. Each control volume consists of a separate liquid and vapor phase. Physics and thermodynamics of each phase and interfacial heat and mass transfer are considered with assumptions for developing the set of equations. The important model assumptions are summarized below.

1. Each phase in a control volume behaves as a continuous stirred tank (CSTs)
2. Ideal gas phase and ideal liquid phase
3. Interfacial mass transfer of only H₂O and CO₂ are considered
4. Only the reactions in the liquid phase are of importance
5. Linear pressure drop along the column
6. The packing height of the column is considered
7. The specific area of the packing material is taken as the effective contact area between the gas and liquid phases
8. Constant volume flow of vapor and liquid is considered
9. Heat loss to the surroundings is neglected

2.1. Main model equations

The main model equations consist of the molar (component) and energy balances for the liquid and vapor phases. The component balances for the gas and liquid phases are respectively:

$$\frac{dc_i^l}{dt} = \frac{u^l}{h_L} \frac{dc_i^l}{dz} + \frac{1}{h_L} \dot{n}_{i,t}^m + \dot{n}_{i,g}^m \quad (1)$$

$$\frac{dc_i^v}{dt} = -\frac{u^v}{(1-h_L)} \frac{dc_i^v}{dz} - \frac{1}{(1-h_L)} \dot{n}_{i,t}^m \quad (2)$$

where c_i is the concentration of component i , t is the time, u is the velocity, h_L is the liquid hold up of the column, dz is the height of a control volume and \dot{n}_i^m is the volumetric molar flow or generation. The superscripts l and v and the subscripts t and g stand for the liquid and vapor phases and the interfacial transfer and the rate of generation, respectively.

The energy balances for the liquid and vapor phases are

$$\frac{dT^l}{dt} = \frac{u^l}{h_L} \frac{dT^l}{dz} + \frac{h_{ov} A_w}{h_L \rho^l \hat{C}_p^l} (T^v - T^l) + \frac{\dot{n}_{CO_2,t}^m}{h_L \rho^l \hat{C}_p^l} (-\Delta H_{ab}) + \frac{\dot{n}_{H_2O,t}^m}{h_L \rho^l \hat{C}_p^l} (-\Delta H_{vap}) \quad (3)$$

$$\frac{dT^v}{dt} = -\frac{u^v}{(1-h_L)} \frac{dT^v}{dz} - \frac{h_{ov} A_w}{(1-h_L) \Sigma(c_i^v \tilde{C}_p^v)} (T^v - T^l) \quad (4)$$

respectively. Here T is the temperature, h_{ov} is the overall heat transfer coefficient between the two phases, A_w is the effective contact area between the phases, ρ is the density and C_p is the specific heat capacity. The symbols \wedge and \sim denote the mass basis and the molar basis, while $(-\Delta H_{ab})$ and $(-\Delta H_{vap})$ represents the heat of absorption of CO₂ and heat of condensation of H₂O.

The MEA solvent system is considered for the analysis, so that the thermodynamic and physical parameters are given accordingly.

2.2. Interfacial mass transfer

Transfer of N₂, O₂ and MEA between the phases has been considered to be negligible. H₂O and CO₂ transfer is allowed for both directions between the phases, and the fluxes are given by the following relation:

$$\dot{n}_{i,t}'' = K_{i,ov}^v A_w (c_i^v - c_i^{v*}) \quad (5)$$

where, K_{ov} is the overall mass transfer coefficient and the superscript v^* represents the concentration at a hypothetical equilibrium state. The concentrations at the hypothetical equilibrium state are found using the saturation vapor pressure for H₂O and Henry's law for CO₂. Correlations for saturation vapor pressure for water and Henry's law coefficient are given by Austgen et al. and the Kent-Eisenberg model [5, 6].

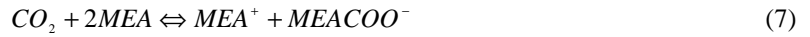
The overall mass transfer coefficient represents the effect from both the liquid side resistance and vapor side resistance on the mass transfer. For H₂O the liquid side resistance is assumed to be negligible, so that the overall mass transfer coefficient is replaced with the local gas side mass transfer coefficient. For CO₂ the overall mass transfer coefficient is given by the following relation:

$$K_{CO_2,ov}^v = \frac{1}{\left(\frac{1}{k_{CO_2}^v}\right) + \left(\frac{H_{CO_2}}{k_{CO_2}^l E}\right)} \quad (6)$$

Here k_i is the local mass transfer coefficient, H_i is the Henry's law coefficient and E is the enhancement factor. The enhancement factor is used in equation (6) in order to represent the effect from the reactions on the mass transfer rate and the value is found from the correlation presented by Hoff. [7]. Local mass transfer coefficients are calculated using the correlation presented by Onda et al. [8].

2.3. Reaction kinetics and phase equilibrium

The reaction kinetics is important for introducing the rate of specie generation to the model and the phase equilibrium is important for interfacial mass transfer. The equilibrium reaction constants and the phase equilibrium are represented according to the Kent-Eisenberg model [6]. Only the overall reaction between MEA and CO₂ is in use for computing the rate of specie generation:



where MEA⁺ is the protonated amine and MEACOO⁻ is the carbamate ion formed from MEA. The forward reaction rate coefficient is introduced as a correlation found from Jamal et al. [9], while the equilibrium coefficient for the overall reaction is found as a combination of the coefficients available with the Kent-Eisenberg model [6].

2.4. Physical properties and other parameters

Physical properties and other parameters are introduced to the model either as correlations or constant values found in the literature, or else using well known calculation methods. Some of the important physical properties and other parameters are given in Table 1 with there literature sources.

Table 1: Some of the physical properties and other parameters used in the MATLAB absorber model.

Property	Source	Comments
Liquid density & Specific heat capacity	Cheng et al. [10]	Effect of CO ₂ in liquid is not considered.
Liquid diffusivity of CO ₂	Versteeg et al. [11]	N ₂ O analogy is used.
Liquid holdup	Billet et al. [12]	

Overall heat transfer coefficient between phases	Cussler et al. [13]	Chilton-Colburn analogy is used.
Heat of absorption of CO ₂	Khol et al. [14]	
Heat of vaporization of H ₂ O	Kvamsdal et al. [4]	

2.5. Numerical method

The model is implemented in MATLAB and the solver ODE15s is used to solve the set of differential and algebraic equations. The 50 control volumes are of uniform size.

3. Simulations

3.1. Steady state simulations

The steady state predictions of the dynamic model are compared with some of the data published by Dugas [15] from a pilot plant study performed taking a 32.5 %wt MEA solution as the solvent system. The column and packing material data for the pilot plant absorber are given in Table 2:

Table 2: Absorber column and packing material data.

Column diameter	0.43 m
Height of packing	6.1 m
Packing type	IMTP-40

Three cases from the pilot plant study (cases 32, 43 and 48) are selected for the steady state result comparison. Since the specific area of the packing material is used as the effective contact area and the measurements of the gas flow into the absorber are claimed to be uncertain (as provided by Kvamsdal et al. [4]), the packing height and the gas flow rate are adjusted in the MATLAB simulations in order to get the same removal efficiencies as what is obtained in the pilot plant. The input data for the input streams and the other parameters that are used in the comparison are given in Table 3.

Table 3: Input data and simulated results (packing height of the pilot plant column is 6.1 m).

Case no:	Inlet liquid temp: [K]	Inlet gas temp: [K]	Inlet liquid rate [m ³ /s]	Inlet gas rate [mol/s]		Packing height [m] (Adjusted)	CO ₂ removal %	
				Measured	Adjusted		Pilot plant	Simulated
32	314	320	$6.8 \cdot 10^{-4}$	3.52	3.70	4.1	95	95.3
43	313	327	$6.6 \cdot 10^{-4}$	5.28	6.90	7.1	72	72.1
48	313	332	$5.0 \cdot 10^{-4}$	5.05	3.95	7.1	69	68.5

The simulated data and the pilot plant data of the temperature profiles along the tower are presented in Figures 1 – 3 for the cases 32, 43 and 47, respectively.

The simulated profiles are in good agreement with the trend of the experimental data points even though the model predictions of temperature seem to be higher compared to experimental data. A possible reason for the deviation could be the negligence of the heat loss to the surroundings from the tower in the MATLAB model. Further, use of the correlation by Cheng et al. [10] to produce the specific heat capacity value for the MEA solution, which is claimed to be having a higher value than expected by Kvamsdal et al. [4], can also have an effect on the results.

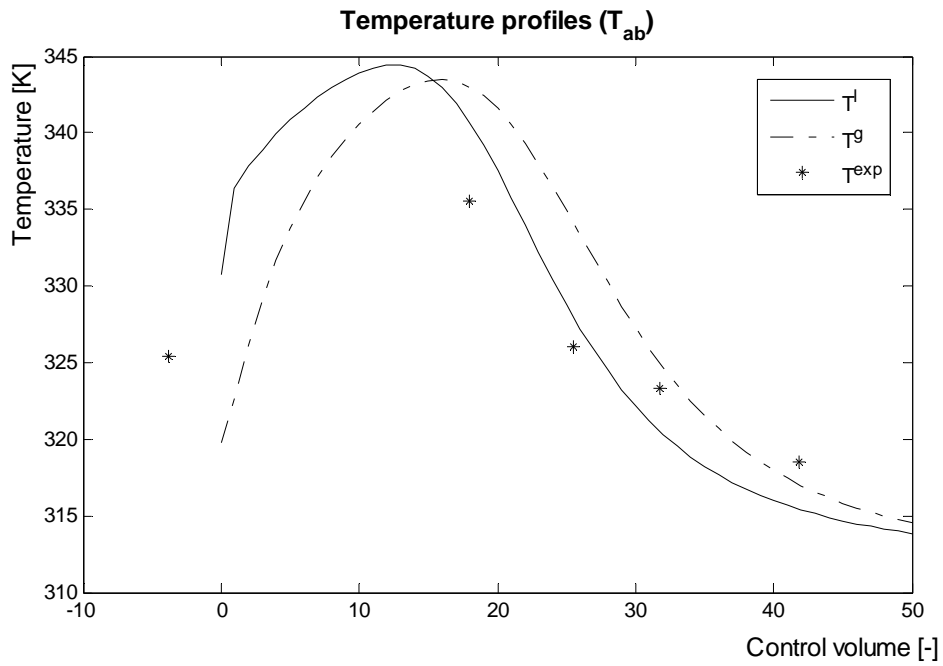


Figure 1: Simulated and experimental temperature profiles for case 32.

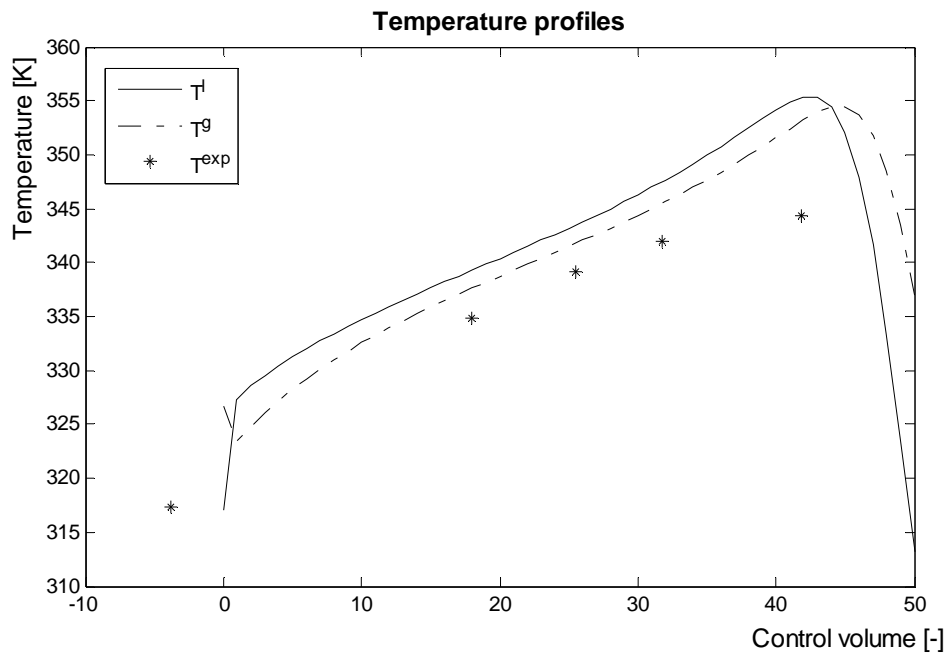


Figure 2: Simulated and experimental temperature profiles for case 43.

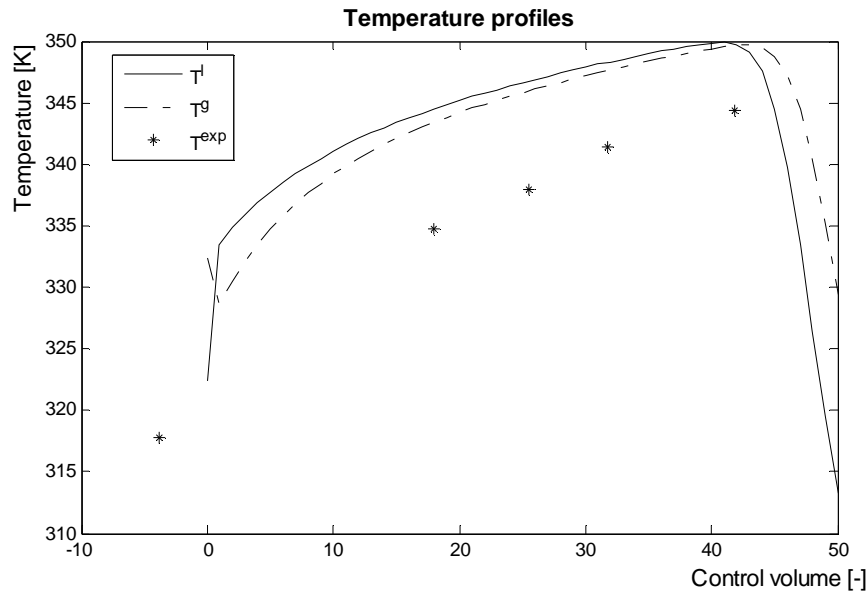


Figure 3: Simulated and experimental temperature profiles for case 47.

A sensitivity analysis is done to check the effect on the simulated temperature values from the used specific heat capacity value. According to the authors' findings, the specific heat capacity value seems to be too high in cases with high CO_2 loadings and too low in cases with low CO_2 loadings along the tower. This needs to be studied further before coming to a conclusion, and will be a point of improvement of the model.

3.2. Dynamic simulations

The dynamic simulations are performed focusing on an excitation of an input. A possible situation in a real plant is to have a varying load in the power plant resulting in varying gas flow into the absorption tower. Such a situation is studied to check the ability of the model to handle a transient condition and achieve a new steady state. The steady state achieved in case 32 is taken as the reference steady state and the gas flow is increased introducing a step change from 3.7 (mol/sec) to 5.7 (mol/sec) after 120 seconds.

In analysis of the dynamic predictions, the CO_2 removal rate, the rich loading and the liquid phase temperature inside the tower are focused upon. In Figures 4 and 5, the change of the CO_2 removal rate and the change of the rich loading value with the time are given. Figure 6 shows liquid temperature profiles at different occasions of the simulation: at the first steady state, 25 seconds after the excitement of the flow and after reaching the new steady state.

4. General Discussion

The model presented here is to some extent a simplified model compared to the models e.g. available with Aspen plus. Though this dynamic model is simpler than some of the available steady state simulators, it can be good enough for control applications.

In addition, some of the assumptions made for the dynamic model may not be realistic for dynamic predictions of the plant behavior. Specifically, the assumption of the constant pressure drop along the tower can cause adverse effects on the dynamic predictions. Though, it is important to check whether the pressure drop exceeds the capacity limitations of the blower during the dynamic simulations, the adequate correlations are limited. Furthermore, use of the specific instead of effective surface area of the packing may have simplified the model too much, as the effective surface area is a function of the liquid load.

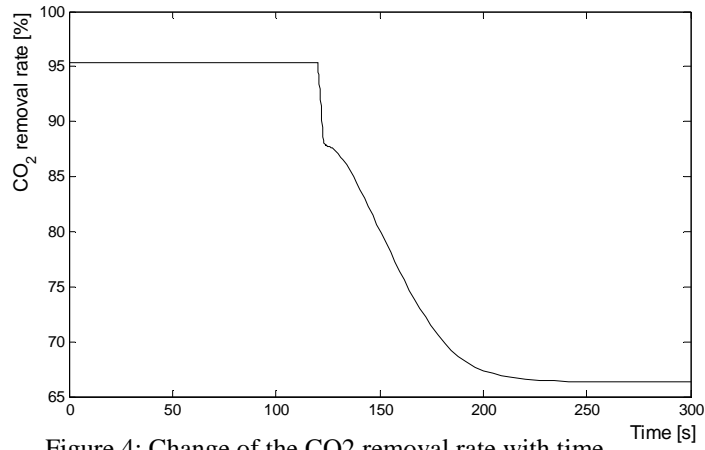


Figure 4: Change of the CO₂ removal rate with time.

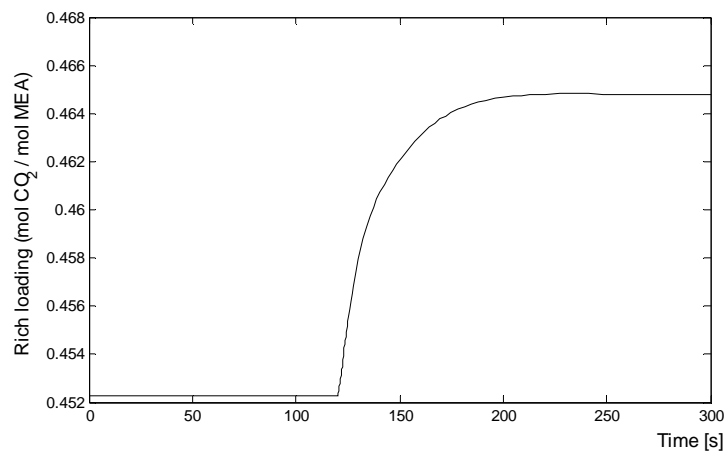


Figure 5: Change in the rich loading with the time.

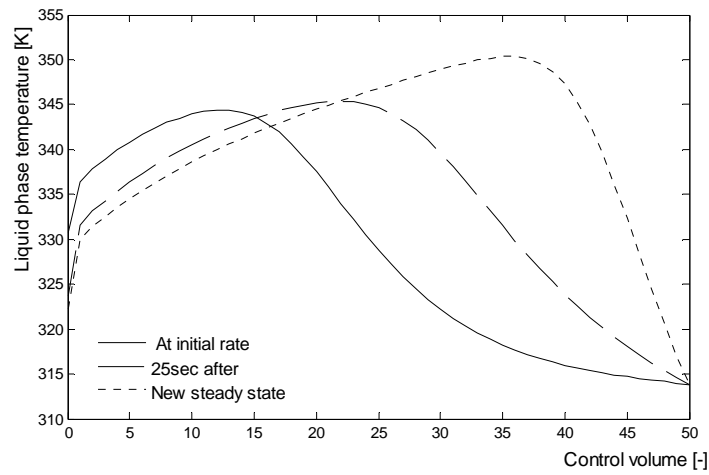


Figure 6: Liquid phase temperature along the tower at different occasions.

Inclusion of only the main reaction between CO₂ and MEA instead of the whole system of reactions that may take place in a CO₂-MEA system can also be considered as a point to be improved in the model though it is being delayed due to the limitation of available reaction kinetic data.

Taking the liquid and vapor phases as ideal phases may not be good enough for a steady state simulator, but could be satisfactory for a dynamic simulator.

5. Conclusions

The importance of a dynamic model is to study the effects from the possible variations of a flue gas source on the absorption plant intended to be used for CO₂ capturing. Having a good dynamic model provides that it is possible for implementing a control system into the corresponding plant.

A dynamic model that is capable of predicting the steady state results reasonably and is able to predict transient conditions and achieve a new steady state after an excitation is developed for the absorption tower of a CO₂ capture plant. The dynamic behavior of the model predictions has to be compared with the behavior of a real plant, which is not done in the current state of the work due to the limitation of available data. The model should expand to cover the whole CO₂ capture plant before developing a control system.

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