

# MODEL BASED CONTROL OF ABSORPTION TOWER FOR CO<sub>2</sub> CAPTURING

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## Abstract

In this work, CO<sub>2</sub> capture by post-combustion using MEA is considered. The mechanistic model for the absorption process is elaborated and includes specie and energy balances for the liquid and gas phases. Model predictive control is implemented as a control strategy for the absorption column.

**Keywords:** CO<sub>2</sub> capturing, Absorption tower, Dynamic model, Control, MPC

## 1 Introduction

### 1.1 Background for work

Emission of carbon dioxide (CO<sub>2</sub>) and its possible negative effect on the climate has gained much interest lately (IPCC, [1]). Although carbon dioxide has the lowest global warming potential among the greenhouse gases, the emitted amount into the atmosphere is large and continuously increasing. A large amount of the emitted carbon dioxide belongs to the energy sector (power plants etc) where the fossil fuel and natural gas are in use [2].

The capturing of carbon dioxide (CO<sub>2</sub>) to reduce its release into the atmosphere is thus of great interest. Several methods exist to capture carbon dioxide, e.g. the post-combustion, pre-combustion, and oxyfuel methods [3].

This study includes the development of a mechanistic model for the absorption tower of the post-combustion process using MEA (monoethanolamine) to improve the separation. Based on the developed model, predictive control is used to improve the operation of the system.

### 1.2 Previous work

This study is an outgrowth of the work of Hansen [21] on post-combustion. Compared to [21], the following issues are revised: (1) Reaction kinetics between CO<sub>2</sub> and MEA; (2) The vapor-liquid equilibrium model is presented by the Deshmukh-Matter approach; (3) Investigation of the physical properties such as diffusivity and viscosity is performed in detail; (4) The energy and component balances both for the liquid and gas phases; (5) Model based control strategy for the

absorption tower; (6) Model analysis; (7) Model validation against the experimental data.

Beside the base study ([21]), a literature survey is carried out on CO<sub>2</sub> capture by means of alkanolamines in the post-combustion process. Vadya *et al.* [4] performed a comprehensive study on the possible reaction kinetic mechanisms in CO<sub>2</sub>-MEA system. Kohl *et al.* [5] give a detailed overview of the gas purification techniques and methods, provides a large set of experimental data for different absorption liquids. Edali *et al.* [6] studied the reaction kinetics of mixed amine solutions for the carbon dioxide capture. The reactions occurring during the CO<sub>2</sub> absorption are described, and the component balance for different liquid species are given. Aboudheir *et al.* [7] also performed an extensive study on the reaction kinetics involving CO<sub>2</sub> and alkanolamines. Liu *et al.* [8] studied vapor-liquid equilibrium models and gave comparative estimates of the existing VLE models proposed by other researchers for CO<sub>2</sub> – MEA systems. Rochelle and Freguia [9] modeled CO<sub>2</sub> capturing by aqueous amine solutions. The results of model development both for the absorption and stripping are presented. Hoff [10] studied carbon dioxide absorption in a membrane contactor, and developed specie balances for the CO<sub>2</sub> absorption; the energy balance for the absorption process was not included, though. While many publications are written on the reaction kinetics with regard to the CO<sub>2</sub>-MEA system, still there is not enough information with regard to the reaction kinetics data, and there is little compliance among the researches about the reaction mechanism. Different approaches are used to develop specie and energy balances.

Little work appears to be available on the control of absorption towers. This is partially due to the fact that this is only a part of the complete post-combustion set-up.

### 1.3 Overview

The next section gives an overview of the post-combustion CO<sub>2</sub> absorption process. The general flow sheet diagram of the absorption process with corresponding description is given, and the absorption liquids and absorption tower are discussed.

The third section describes development of the distributed mechanistic model for the absorption tower.

The fourth section describes the implementation of MPC for the absorption process control.

The final section of the paper gives a conclusion of the

column. The steam is separated from the gas in the condenser, and it is sent back to the stripper column. CO<sub>2</sub> is compressed and sent to storage. The lean solution at the bottom of the stripper has low CO<sub>2</sub> content and can be used again in the absorption process. From the stripper, the lean solution is

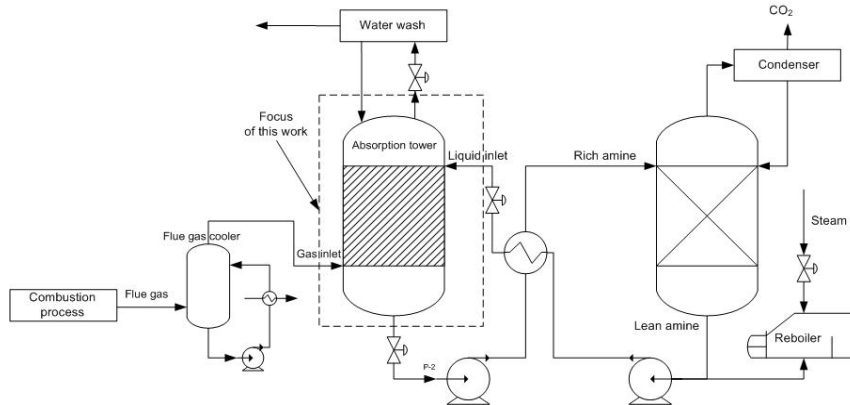


Fig. 1 Absorption/stripping process flow diagram

performed work.

## 2 Process description

Fig. 1 illustrates the basic flow scheme for the alkanolamine acid-gas removal process. For the sake of simplicity, the control elements are skipped in the flow scheme.

The exhaust gas comes from the combustion process and is further cooled, and the cooled gas is fed to the bottom of the absorption tower. The gas rises in the upstream direction meeting a counter current liquid stream coming from the top of the tower. The carbon dioxide diffuses from the gas and into the aqueous amine solution and reacts with MEA (or other alkanolamine), causing the gas stream to become gradually leaner in CO<sub>2</sub> as it propagates upwards in the tower. The purified gas leaves the absorption tower and goes to the water wash (reflux drum): during the absorption process, some amount of amines vaporizes into the gas phase, and a regeneration of these vaporized amines takes place in the water wash. After the water wash step, the regenerated amines are sent back to the absorption tower and the purified gas is released into the atmosphere.

Contrary to the gas, the liquid gets enriched by CO<sub>2</sub> as it flows from the top to the bottom of the absorption tower. At the bottom, the rich CO<sub>2</sub> solution is pumped out from the tower, passed through a heat exchanger and is directed to the top of the second tower – the stripper (or desorber).

The temperature and pressure in the stripper are operated so that reverse chemical reactions take place and CO<sub>2</sub> is stripped from the CO<sub>2</sub> rich aqueous amine solution into the gas phase again. The temperature in the stripper is maintained by generating steam from the bottom reboiler. The gas in the stripper column, which contains steam and CO<sub>2</sub>, is removed from the

pumped through the heat exchanger back to the absorption tower.

In practice, the absorption tower is operated at around 40-55 [°C], and the stripper is operated at 120 [°C]. The exhaust gas coming into the absorption tower has a pressure which is rarely higher than atmospheric pressure (5 [bar]); for natural gas the pressure range is considerably higher, typically at 100 [bar] [5].

There are various types of absorption towers. For this particular study, a packed tower is selected; this choice is inspired by the common usage in the industry. The gasket inside the absorption tower can be classified into *structured* and *random* gaskets. Here, a structured gasket is assumed since the structured gaskets have better mass transfer properties and a lower pressure drop, these being important properties when it comes to energy consumption, cost, and efficiency. Among the available structured gaskets present in the market, the Montz packing of B1 type is selected for the current study.

The absorption liquid for CO<sub>2</sub> capturing can be either physical liquid or chemical solvent. In the industrial scale, chemical liquids are more preferable because of the higher absorption capacity in comparison with the physical absorption liquids. The alkanolamines are found to be the most suitable reactive component in the aqueous absorbent solution for CO<sub>2</sub> capture since they possess many desirable properties. In this study, monoethanolamine (C<sub>2</sub>H<sub>7</sub>NO) is selected as an absorption liquid since it is widely used in the industry and has some advantages over other commercial alkanolamines such as a high absorption rate due to the low molecular weight, a fast reaction rate, and low cost. Along with the advantages, MEA has some deficiencies such as high regeneration costs due to formation of carbamate, relatively high vapor pressure, relatively high corrosivity which limits the

concentration of MEA in aqueous solution to 20% of weight without corrosion inhibitors and up to 30% with them. In spite of these disadvantages, MEA is widely used nowadays for CO<sub>2</sub> capturing, alone or in a mixture with other alkanolamines.

### 3 Modeling and simulation of the absorption tower

#### 3.1 Distributed mechanistic model

In any dynamic system where intensive variables vary both with time and space, a distributed mechanistic model has to be developed in order to reflect the dynamics of the system correctly. To develop the distributed model, the absorption tower is partitioned into infinitesimal small slices or subsystems where each subsystem is assumed to be ideally mixed as shown in Fig. 2. This discretization of the absorption tower will introduce an error, which decreases as the thickness of the slices decrease, Δz→0. The major

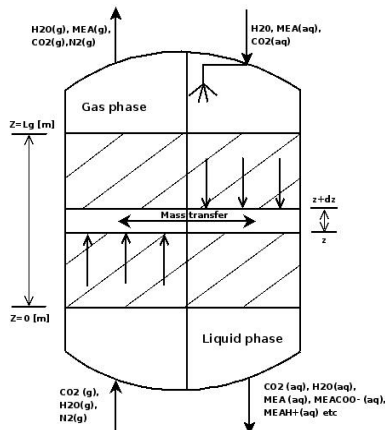


Fig. 2 Sketch of the segregated absorption tower

assumptions introduced are: (1) the flow of the gas and liquid is a plug flow implying no back mixing, (2) the gas velocity is spatially constant and equal to the inlet gas velocity in the current study, (3) the velocity of the mixture of liquid MEA and water is assumed to be spatially constant due to incompressibility of the liquid, (4) initially the liquid phase consists of MEA and water while the gas phase consists of CO<sub>2</sub>, N<sub>2</sub> and water. N<sub>2</sub> is assumed to be nonreactive with the aqueous amine solution, (5) all chemical reactions take place in the liquid phase.

#### 3.2 Vapor-liquid equilibrium

Several theoretical approaches have been developed in order to describe the complex chemical absorption and desorption processes. The stagnant film theory, proposed by Whitman and further extended and implemented by Hatta, is taken as a background to describe the mass transfer of CO<sub>2</sub> into the aqueous amine solution. Fig. 3 depicts the application of two film theory for mass transfer of CO<sub>2</sub> into the amine solution and mass transfer of MEA and water from the

liquid phase into the gas phase. The main assumptions with the two film theory are (1) the existence of an interface between liquid and gas phases, (2) a thin layer of stagnant film on the liquid as well as on the gas side, (3) liquid and gas in turbulent contact with each other, (4) the existence of equilibrium at the interface between gas and liquid. The driving force in the gas phase is the partial pressure difference between partial pressure in the gas-bulk phase and partial pressure at the interface. The driving force in the liquid phase is given by the concentration difference at the interface and in the liquid bulk phase. Since it is not practical to operate with the interfacial partial pressure and concentration, the assumption of equilibrium condition between two phases eliminates the need for the partial pressure and concentration at the interface by using the equilibrium pressure and concentration instead.

$$\begin{aligned} N_A &= k_g (P_A^g - P_A^{g,eq}) \\ N_A &= k_l (C_A^{l,eq} - C_A^l) \end{aligned} \quad (1)$$

Various scientists have attacked the problem of elaborating the vapor-liquid equilibrium model (VLE) for CO<sub>2</sub> absorption from different angles. According to Kohl and Nielsen [5], three main contributions for VLE model development were made by Kent-Eisenberg, Deshmukh-Matter and Austgen *et al.* In the current study, the Deshmukh-Matter approach is selected to describe vapor-liquid equilibrium (VLE) in the CO<sub>2</sub>-MEA system. Briefly, the necessary conditions for the Deshmukh-Matter model are (1) defined equilibrium constants for the reactions, (2) Henry's law constants for CO<sub>2</sub> in water, (3) fugacity

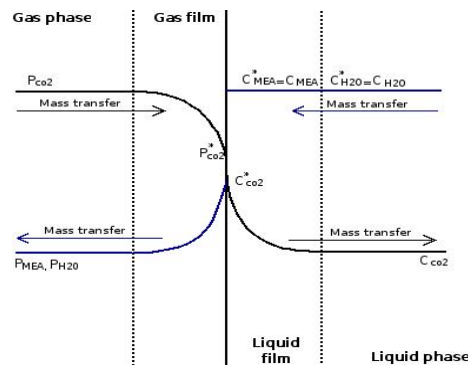


Fig. 3 CO<sub>2</sub> transfer from gas phase to liquid phase.

coefficients for the gas components, and (4) activity coefficients for the liquid components.

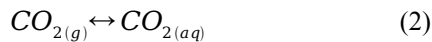
#### 3.3 Reaction kinetics

CO<sub>2</sub> is absorbed into an aqueous amine solution by means of chemical reactions taking place between CO<sub>2</sub> and the amine solution. There are three possible mechanisms that can describe the CO<sub>2</sub> absorption in the amine solution according to the recent review performed by Vaidya [4] and others. These are the *zwitterion mechanism*, the *thermomolecular mechanism*, and the *base-catalyzed hydration*

*mechanism.* To describe reactions emanating in the absorption tower, the thermomolecular mechanism is selected in this work. The thermomolecular mechanism originally proposed by Crooks and Donellan and revised by Svendsen and da Silva [11] implies a single step reaction of CO<sub>2</sub> with one molecule of MEA and water as a base at the same time.

According to Mandal *et al.* [12] and Benamor *et al.* [13], the following reactions emanate in the aqueous amine solution. One phase equilibrium and six chemical equilibria are introduced to describe the chemistry involved in the CO<sub>2</sub> absorption. The main reactions in the absorption tower are defined as

1. Solubility of CO<sub>2</sub>



2. Reaction of MEA and CO<sub>2</sub>



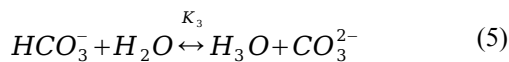
The reaction is reversible and has a finite reaction rate.

3. Bicarbonate formation



The reaction is reversible and has a finite reaction rate.

4. Bicarbonate disassociation



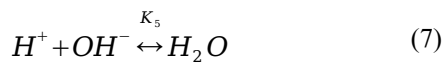
The reaction is reversible, instantaneous and at equilibrium [12].

5. Protonation of MEA



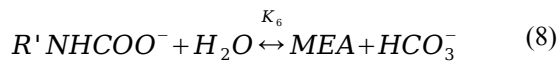
The proton transfer reaction is very fast, instantaneous and at equilibrium as well as reversible, according to Hagewiesche *et al.* [14].

6. Water formation



This reaction is also considered as reversible, instantaneous and at equilibrium.

7. Carbamate reversion



The carbamate reversion is considered to be reversible, instantaneous and at equilibrium.

The reaction of carbon dioxide with water is considered to be very slow and can be neglected, according to [14]. MEA also reacts with oxygen-bearing gases to form degradation products, but those reactions are not in the focus of this study. However, those reactions would be important to define the amine degradation level in the absorption tower and can also be used for quality control purposes.

The empirical correlations for some equilibrium constants, and forward and backwards reaction rate constants, are found in various publications and adjusted in order to be able to use them in this work.

Many authors in related publications concerning the kinetics of the CO<sub>2</sub> absorption tend to combine equilibrium constants of the other reactions in order to find missing ones. An empirical formula for  $K_1$  was not found in scientific publications, and it was obtained by combining equilibrium constants  $K_2$ ,  $K_3$  and  $K_6$  by assuming that at some arbitrary time all reactions will reach chemical equilibrium.

With reference to Mandal *et al.* [12] and Ahmed *et al.* [6], the water can be eliminated from the reactions and from the stoichiometric matrix under the assumption of an infinite dilution. The element H<sub>3</sub>O<sup>+</sup> can be regarded as H<sup>+</sup> according to [6].

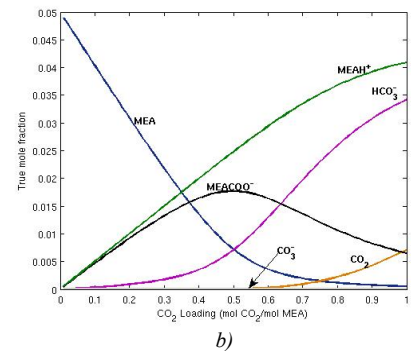
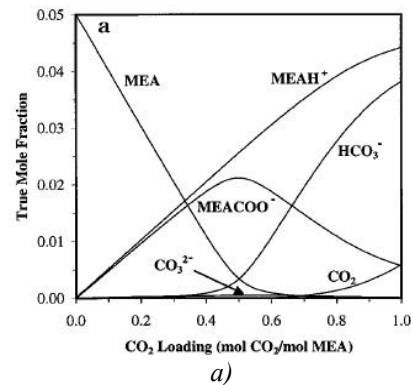


Fig. 4 Specie concentration plot for 15% MEA and  $T_L=40^\circ\text{C}$ .

a) reported by Liu [8], b) this study

Fig. 4 shows specie concentration plot of this study and reported. Fig. 4 reflects the change in mole fraction of the liquid species with regard to the loading of carbon dioxide to MEA.

### 3.4 Mass transfer coefficients

In order to elaborate the total mass transfer coefficient for CO<sub>2</sub> and find the expression for mass transfer, a mole balance was performed for the interface between the gas and liquid phases. Mass transfer is defined as follows

$$N_{CO_2} = K_{G,CO_2} (P_{CO_2}^g - \zeta_A H_{CO_2} C_{CO_2}^l) \quad (9)$$

where  $K_{G,CO_2}$  is total mass transfer coefficient

$$K_{G,CO_2} = \frac{1}{\left( \frac{H_{E,CO_2}}{E k_l a_{gl}} + \frac{RT^g}{k_g a_{gl}} \right)} \quad (10)$$

The salting-out effect is an indicator of the deviation from an ideal behavior of the liquid mixture. In order to take into account the salting-out effect, Eq. (9) is modified by adding  $\zeta_A$ . Here,

$$\zeta_A = \left( \frac{H_A}{H_A^s} \right) = 10^{h_A I} \quad (11)$$

The enhancement factor is introduced in Eq. (10) in order to allow reactions to take place at the liquid film.

The elaboration of the total mass transfer coefficient for both MEA and H<sub>2</sub>O is similar to the one with CO<sub>2</sub>. However, under the assumption of a well mixed liquid phase, the equilibrium concentration both for MEA and H<sub>2</sub>O can be taken equal to the liquid bulk concentration of MEA and H<sub>2</sub>O respectively (i.e.

$C_{MEA}^{l,eq} \approx C_{MEA}^l, C_{H_2O}^{l,eq} \approx C_{H_2O}^l$ ). In other words, the absence of liquid film is assumed, whereas there is present a gas film on the gas phase side (Fig. 3). MEA and H<sub>2</sub>O are considered to be volatile components and they are likely to evaporate into the gas phase. Mass transfer in the gas phase for MEA is given as

$$N_{MEA} = K_{G,MEA} (P_{MEA}^{g,eq} - P_{MEA}^g) \quad (12)$$

and for water is given as

$$N_{H_2O} = K_{G,H_2O} (P_{H_2O}^{g,eq} - P_{H_2O}^g) \quad (13)$$

The development of mass transfer for MEA and water can be accomplished under non-ideal behavior of the gas phase. Instead of using Henry's approximation to describe the vapor-liquid equilibrium, which implies a linear relationship between partial pressure and concentration at equilibrium, the vapor-liquid equilibrium can be expressed using fugacities of each of the phases. In order to find the equilibrium partial pressures for MEA and water as well as the partial pressure of MEA and water in the gas phase, the fugacity can be introduced as a function of partial pressure. The driving force for molecules of water and MEA to evaporate to gas phase, can be presented as the fugacity difference between fugacity at the interface and fugacity in the bulk side of the gas as if

$$\begin{aligned} N_{MEA} &= K_{G,MEA} (f_{MEA}^{V,eq} - f_{MEA}^V) \\ N_{H_2O} &= K_{G,H_2O} (f_{H_2O}^{V,eq} - f_{H_2O}^V) \end{aligned} \quad (14)$$

The fugacity coefficients are found by using the Peng-Robinson equation of states for the vapor side and the activity coefficients are determined by the Wilson equation.

### 3.5 Gasket properties

The mass transfer coefficient both for liquid and gas depends on the type of chosen packing design for the absorption tower. Billet [15] provides the empirical expressions for the mass transfer coefficients for the

gas and liquid sides, and for the various types of packings. Those expressions require some knowledge of the physical properties of both gas and liquid in the absorption tower. In order to find overall gas viscosity, the Hering-Zipperer correction to the Wilke's equation is applied [16]. Diffusivity of water and carbon dioxide in the gas phase is found using the Chapman-Enskog equation. Diffusivity of MEA in the gas phase can be found using an equation given by Fuller et al. [16]. To find the diffusivity of CO<sub>2</sub> in the aqueous amine solution, a CO<sub>2</sub>-N<sub>2</sub>O analogy is applied ([17], [18], [8]) and estimated by the expression proposed by Snijder et al. [17]. The diffusivity of CO<sub>2</sub> in the water is found by the expression suggested by Versteeg and Swaaj [19].

### 3.6 Component balances

The expression for the concentration of CO<sub>2</sub> in the liquid phase is based on the mole balance. The specie balances for CO<sub>2</sub> in the liquid, MEA, and water are

$$\frac{\partial C_{CO_2}^l}{\partial t} = -u_l \frac{\partial C_{CO_2}^l}{\partial z} + N_{CO_2} - r_1 - r_2 \quad (15)$$

$$\frac{\partial C_{MEA}^l}{\partial t} = -u_l \frac{\partial C_{MEA}^l}{\partial z} - N_{MEA} - r_1 - r_4 + r_6 \quad (16)$$

$$\frac{\partial C_{H_2O}^l}{\partial t} = -u_l \frac{\partial C_{H_2O}^l}{\partial z} - N_{H_2O} \quad (17)$$

The specie balances for the six ionic species in the liquid phase are also developed.

The specie balances for the gas phase is similar to the ones in the liquid phase. The dynamic expression for CO<sub>2</sub> in the gas phase can be written as

$$\frac{\partial C_{CO_2}^g}{\partial t} = -u_g \frac{\partial C_{CO_2}^g}{\partial z} - N_{CO_2} \quad (18)$$

and similarly for MEA

$$\frac{\partial C_{MEA}^g}{\partial t} = -u_g \frac{\partial C_{MEA}^g}{\partial z} + N_{MEA} \quad (19)$$

and for water

$$\frac{\partial C_{H_2O}^g}{\partial t} = -u_g \frac{\partial C_{H_2O}^g}{\partial z} + N_{H_2O} \quad (20)$$

### 3.7 Energy balances

To be able to reflect the change in temperature both in the liquid and gas phases, the corresponding energy balances are developed. The heat transfer between the liquid and gas phase is found assuming external turbulent forced convective flow over a flat plate [20]. The temperature model for the liquid phase is of the form

$$\frac{\partial T^l}{\partial t} = -u_l \frac{\partial T^l}{\partial z} - \frac{\sum_j (-\Delta \tilde{H}_{rj} r_j)}{\sum_j (C_j^l \tilde{c}_{p,j}^l)} - \frac{\sum_j N_j}{\sum_j (C_j^l \tilde{c}_{p,j}^l)} \Delta \tilde{H}_v - \frac{a_{g/l} h_g (T_{z+\Delta z}^l - T_{z+\Delta z}^g)}{\sum_j (C_j^l \tilde{c}_{p,j}^l)} \quad (21)$$

The temperature model for the gas phase is of form

$$\frac{\partial T^g}{\partial t} = -u_g \frac{\partial T^g}{\partial z} + \frac{a_{g/l} h_g (T_{z+\Delta z}^l - T_{z+\Delta z}^g)}{\sum_j (C_j^g \tilde{c}_{p,i}^g)} \quad (22)$$

**3.8 Exhaust gas simulation**

The input data for the simulation is calculated on the basis of 400 MW power plant with the annual

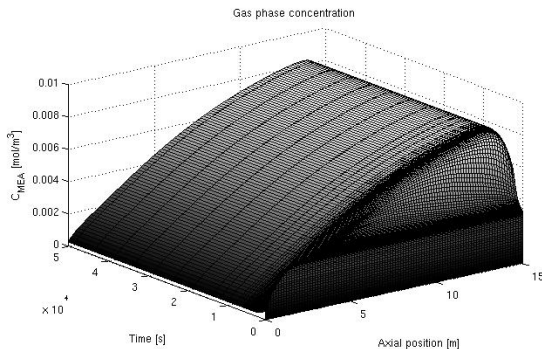


Fig. 5 Concentration of MEA in the gas phase

emission of CO<sub>2</sub> equal to one million tons. The partial derivatives are solved by converting them into ordinary derivative equations by the MOL (Method of Lines). The simulation of the absorption tower is calculated for 50000 sec (ca. 14 hours and 20 min).

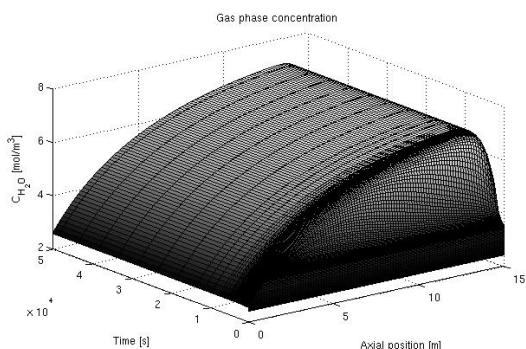


Fig. 6: Concentration of water in the gas phase

The liquid flow rate is selected to be 0.81 [m<sup>3</sup> s<sup>-1</sup>] and the height of the absorption column equals to 15 [m]. The hydraulic retention time is calculated to be 3000 [s] or approximately 50 [min]. Fig. 5 illustrates the concentration of MEA in the gas phase. From the

figure it can be observed that the concentration of MEA in the gas phase starts to increase as the gas propagates from the inlet to the outlet of the absorption tower. However, near the top of the absorption tower (L=14 [m]) the concentration starts to decrease slightly since the gas temperature decreases at L=14 [m] (the fugacity is dependent on the temperature). The increase and decrease of MEA in the gas phase are stipulated by the mass transfer between the liquid and gas phases caused by the fugacity difference. The fugacity difference defines the direction of diffusion whether the diffusion occurs from the gas phase into the liquid or vice versa.

Fig. 7 depicts the concentration of CO<sub>2</sub> in the exhaust gas. As can be seen from the figure, the concentration of CO<sub>2</sub> decreases as the gas goes from the inlet to the outlet of the absorption tower. Some amount of CO<sub>2</sub> is diffused into the aqueous amine solution driven by the concentration difference in the gas and liquid phases. According to the figure, the CO<sub>2</sub> concentration at the inlet equals to 1.47 [mol m<sup>-3</sup>] and at the outlet the concentration is reduced down to 0.13 [mol m<sup>-3</sup>]

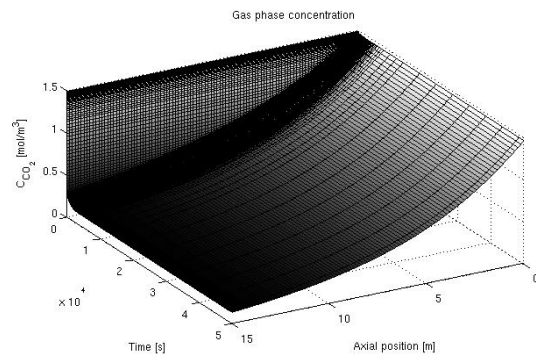


Fig. 7 Concentration of CO<sub>2</sub> in the gas phase

which is approximately 91.09% removal.

Fig. 8 shows the distributed concentration of MEA in the liquid phase. The concentration of MEA in the liquid drops as the aqueous amine solutions flows from the top of the tower to the bottom. The decrease

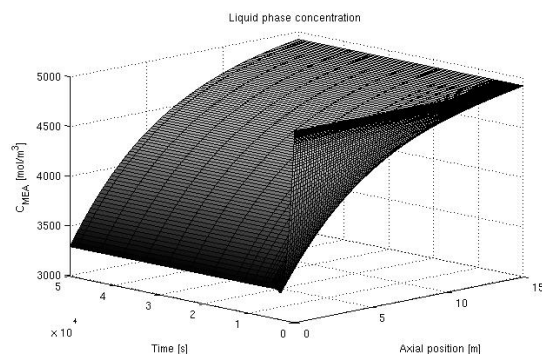


Fig. 8 Concentration of MEA in the liquid phase

of MEA in the liquid phase can be explained in two ways: (1) a significant amount of MEA reacts with diffused CO<sub>2</sub> in the liquid producing additive products such as bicarbonate, carbamate, etc.; (2) a small part of MEA vaporises into the gas phase.

Fig. 12 illustrates the concentration of CO<sub>2</sub> in the liquid phase. The concentration of CO<sub>2</sub> is almost zero and starts to increase insignificantly (up to  $2.3 \cdot 10^{-5}$  [mol m<sup>-3</sup>]) as liquid flows from the top to the bottom of the tower. The comparatively high concentration of CO<sub>2</sub> at the bottom of the tower is explained by the high concentration of CO<sub>2</sub> in the gas phase at the inlet of the tower. Since the VLE is given by Henry's law for CO<sub>2</sub>, it requires the concentration of CO<sub>2</sub> in the liquid to be equal to the partial pressure of CO<sub>2</sub> in the gas phase at equilibrium. As carbon dioxide diffuses into the liquid, it is consumed in the reactions with MEA and hydroxide which leads to virtually zero

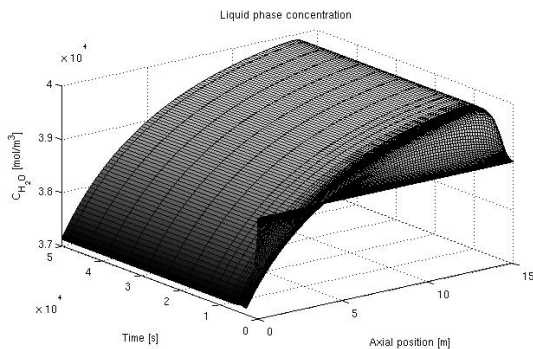


Fig. 9 Concentration of water in the liquid phase

( $6.6 \cdot 10^{-7}$  [mol m<sup>3</sup>]) concentration of free CO<sub>2</sub> in the aqueous amine solution. Fig. 6 displays the concentration of water in the gas phase. The concentration of water in the aqueous amine solution is depicted in Figure 9.

The liquid and gas temperatures are displayed in Fig. 10 and 11, respectively.

The liquid temperature starts from 318 [K] (45°C) on the top of the absorption tower and then increases due to the heat transfer from the gas to liquid, heat of reaction due to the chemical absorption of CO<sub>2</sub> into the amine solution, latent heat of vaporization and/or condensation due to the particle diffusion. Near the top of the tower (L=14 [m]) the liquid reaches its maximum temperature of 330.9 [K] (57.9 °) and the temperature then starts to decrease as liquid flows from the top to the bottom of the tower transferring

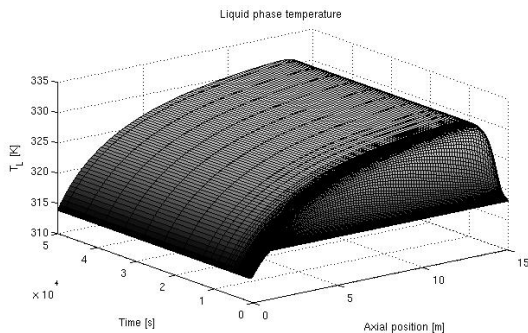


Fig. 10 Liquid phase temperature

the heat to the gas.

The gas coming to the absorption tower has a temperature of 313 [K] (40°C). As the gas comes in contact with the liquid, the temperature of the gas increases due to the heat transfer from the liquid to the gas since the liquid has a higher temperature than the gas. Near the top of the absorption tower (L=13) the

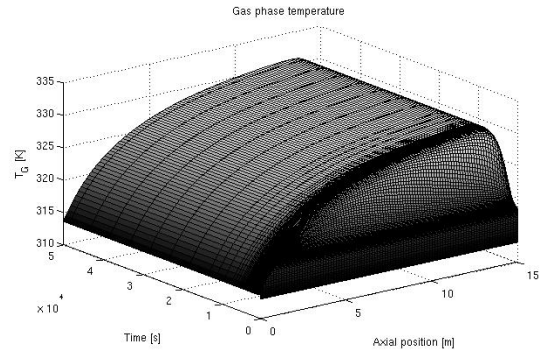


Fig. 11 Gas phase temperature

gas temperature reaches its maximum temperature of 330.9 [K] (57.9°C). The decrease of the gas temperature on the top of the absorption tower can also be observed since the liquid coming into the tower has a lower temperature, and the heat is transferred from the gas to the liquid causing the temperature of liquid to increase.

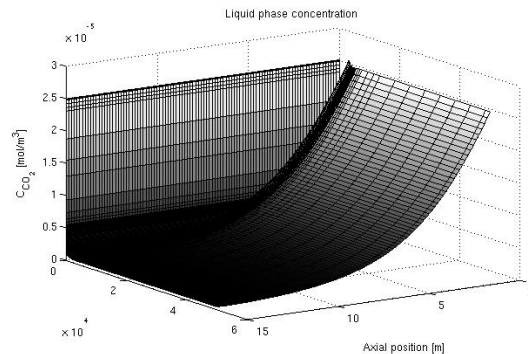


Fig. 12 Concentration of CO<sub>2</sub> in the liquid phase.

#### 4 Process control

The design of the control strategy for the CO<sub>2</sub> absorption process requires to take into consideration

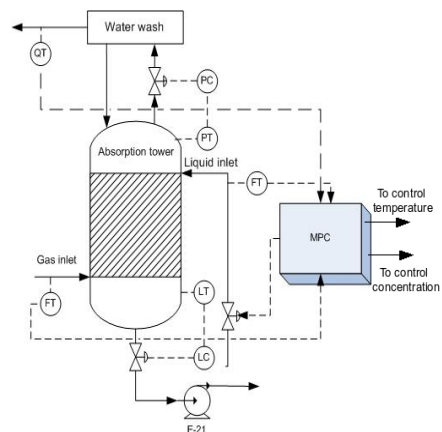


Fig. 13 MPC for the absorption tower control.

the whole process in order to avoid undesirable effects during the plant operation and to attain satisfactory performance. Looking at the process as a whole will ensure secure, stable and reliable operational conditions and also points out at the potential disturbances and miscellaneous control problems. This study is focused only on the control of the absorption process, as an initial study.

#### 4.1 MPC

In order to be able to implement MPC to control the

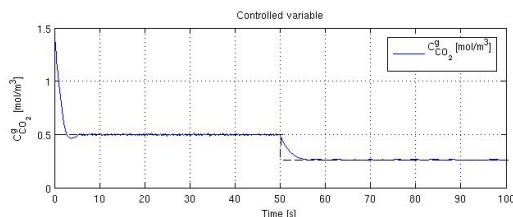


Fig. 14 Step change in the setpoint

absorption tower, the physical model of the absorption tower was linearized numerically around the operating points due to the complex nature of the developed model. Fig. 13 shows schematically MPC for the absorption tower control. The output variable or controlled variable represents the direct measure of quality and process performance. The controlled variable in the case of the absorption tower is the concentration of  $\text{CO}_2$  at the exit of the tower. Another possible controlled variable could be the concentration of MEA degradation products; however this is beyond the current study. The MPC for the mathematical model of the absorption tower is calculated using Model Predictive Control Toolbox in MATLAB, which provides graphical interface to the MPC calculation routines.

The input variables or manipulated variables are the liquid velocity, the liquid concentration of MEA and the liquid temperature. However, the liquid temperature and the content of MEA in the liquid phase have to be manipulated through the stripper which is not in the scope of the this study. The large influence on the controlled variable comes from liquid velocity in the absorption tower.

The disturbances affecting the absorption process significantly are the inlet content of  $\text{CO}_2$  (gas composition), the inlet gas temperature (fluctuation of gas temperature) and the inlet gas velocity; these variables can not be considered as manipulated variables since they depend on external processes (eg. combustion process).

During the simulation of the mechanistic model, the upper and lower limits for the liquid velocity is found. The minimum liquid velocity is determined to be  $0.001 \text{ [m s}^{-1}\text{]}$  and the maximum liquid velocity is determined to be  $0.009 \text{ [m s}^{-1}\text{]}$ ; this is subject to constraint the input variable which is the liquid velocity. Since the input variable is constrained, one

should remember to avoid to give large steps in the set point.

The temperature of the liquid and MEA concentration in the liquid are also defined as manipulated variables. These variables are also constrained to keep the temperatures in the range of absorption process and avoid reverse reactions.

The prediction horizon is selected to be 10 and the control horizon to be equal to 5. The MPC controller based on the linearized model is simulated to control the non-linear system.

Fig. 14 depicts the performance of MPC during a given step change to the set point: decreasing  $\text{CO}_2$  content in the gas phase from  $0.5 \text{ [mol m}^{-3}\text{]}$  to  $0.3 \text{ [mol m}^{-3}\text{]}$ . As it can be seen from Figure 14, the process variable follows the set point after the applied step change, sufficiently good.

It is of interest to give some change in the disturbance variables and observe how the MPC compensates for the applied disturbances. The disturbances such as inlet gas velocity, gas temperature and inlet content of  $\text{CO}_2$  in the gas can be regarded as measured disturbances, and a feed forward to the MPC can be used. The inlet gas content of  $\text{CO}_2$  at time 50 [s] is increased in a step change from  $1.47 \text{ [mol m}^{-3}\text{]}$  up to  $1.97 \text{ [mol m}^{-3}\text{]}$ , the inlet gas temperature is increased to 1 [K] and gas velocity is changed from  $3 \text{ [m s}^{-1}\text{]}$  to  $3.5 \text{ [m s}^{-1}\text{]}$ . Figure 15 illustrates the compensation for the measured disturbances.

The disturbances are applied in different time instances. As it can be observed, all disturbances are well attenuated; the process variable does not deviate much from the set point.

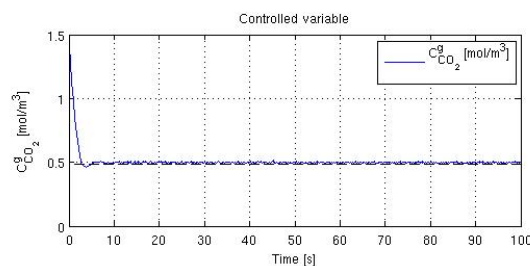


Fig. 15 Disturbance compensation abilities

## 5 Discussion and conclusions

The absorption is an inherently complex process which depends on various factors such as reaction kinetics, physical properties of the fluid, temperature, mass transfer, etc. The two film theory is used to describe the absorption process. The vapor-liquid equilibrium model for  $\text{CO}_2$  is approximated by the Henry's law approach, for MEA and water the concept of fugacity and activity coefficient is introduced. The fugacity coefficient is depended on the temperature, binary interaction parameters and mixing rules for MEA-water system. The activity coefficient also has strong dependency with the temperature and the



Wilson coefficients which are defined experimentally for MEA-water system. The fugacity coefficients for MEA and water in the gas phase are calculated by implementing the Peng-Robinson equation of state, the activity coefficients for MEA and water in the liquid phase are found using the Wilson's equation. The driving force for molecules of water and MEA to diffuse from the one phase to other is assumed to be fugacity. The driving force for the CO<sub>2</sub> molecule migration from one phase to the other is defined as concentration difference between the phases. The mass transfer coefficients for CO<sub>2</sub>, MEA and water are developed based on the mass balance. A comprehensive study is performed to investigate properties of the liquid and gas such as viscosity, diffusivity, density, thermal conductivity, heat capacity, chemical and equilibrium constants, Henry's constants, heat of reaction, various mixing rules, etc.

A study on reaction kinetics is carried out. The generally accepted "zwitterion mechanism" is not used in the model, instead the "thermo molecular mechanism" is chosen to explain the reactions in the absorption process. This mechanism is a single step reaction mechanism that eliminates the formation of zwitterion as an intermediate state. The reactions emanating as a result of CO<sub>2</sub> absorption in the aqueous amine solution are specified and corresponding reaction kinetics data are found. The reaction kinetics is validated according to the reported data in publications by plotting the specie concentration. The reaction kinetics is taken into account in specie and energy balances. The gasket properties are studied in detail.

The specie balance is developed for the gas and liquid phases, including the corresponding balances for the ionic species.

The energy balance is elaborated both for the gas and liquid phases. The latent heat of vaporization is included along with the heat of reaction and the heat transfer into the energy balance. The latent heat of vaporization/condensation is defined only for MEA and water. The heat of reaction is taken only for the reaction of MEA and CO<sub>2</sub> since the large amount of heat comes from that reaction.

The obtained model for the CO<sub>2</sub> absorption is simulated. The results of simulation shows satisfactory results. 91.09% of the carbon dioxide removal from the exhaust gas is achieved with the height of absorption tower equal to 15 [m] and the liquid velocity 0.005 [m s<sup>-1</sup>] (or 0.81 [m<sup>3</sup> s<sup>-1</sup>]).

The developed mathematical model of the absorption tower is compound of several nonlinear elements acting in combination with each other in the model and causing high nonlinearity. Indeed, calculation of the fugacities, where the cubic equation of state is involved, the various empirical expressions to find the reaction rates, the nonlinear formulas to define the physical properties of the gas and liquid, mixing rules and other formulas and expressions. The high

nonlinearity can be a serious obstacle for the model linearization. For control synthesis, the nonlinear model is linearized around the operating points. The numerically linearized model contains positive poles one of the explanation for it might be the presence of the exothermal chemical reactions and different reaction time for certain reactions. In order to be able to use the linearized model in MPC, the linearized model was numerically separated into the stable and unstable parts in MATLAB. The stable part is then used in MPC for the absorption tower control.

Model predictive control is implemented to control the absorption tower. The MPC showed good results for the disturbance attenuation, and was able to handle relatively large changes in set point and disturbance variables. Tuning of the MPC is performed by adjusting corresponding weighting matrices. In spite of using the reduced linearized model in MPC to control the physical model of the absorption tower it was possible to run simulation of the nonlinear model with MPC for 100 [s] and achieve satisfactory results. Further study is expected regarding the MPC for the absorption tower .

## Nomenclature

$a_{g/l}$	interfacial area between gas and liquid,	$\left[ \frac{m^2}{m^3} \right]$
$k_g$	gas mass transfer coefficient,	$\left[ \frac{m}{s} \right]$
$k_l$	liquid mass transfer coefficient,	$\left[ \frac{m}{s} \right]$
$u_l$	liquid velocity	$\left[ \frac{m}{s} \right]$
$u_g$	gas velocity	$\left[ \frac{m}{s} \right]$
$r_i$	rate of reaction	$\left[ \frac{mol}{m^3 s} \right]$
$C^l$	liquid phase concentration	$\left[ \frac{mol}{m^3} \right]$
$C^g$	gas phase concentration	$\left[ \frac{mol}{m^3} \right]$
$E$	enhancement factor	
$f^o$	fugacity in the vapor phase	[kPa]
$H_E$	Henry's constant	$\left[ \frac{m^3 kPa}{mol} \right]$
$H_A^s$	Henry's constants for the electrolyte solution	$\left[ \frac{m^3 kPa}{mol} \right]$
$H_A$	Henry's constant for molecular solvent at the same temperature profile	$\left[ \frac{m^3 kPa}{mol} \right]$
$h_A$	sum of the contribution from positively, and	$\left[ \frac{l}{mol} \right]$

	negatively charged ionic species and attributed to dissolved gas	
$h_g$	heat transfer coefficient for the gas phase,	$\left[ \frac{J}{m^2 K s} \right]$
$\tilde{c}_{j,p}^l$	specific heat capacity in constant pressure for specie i in the liquid phase.	$\left[ \frac{J}{mol K} \right]$
$\tilde{c}_{j,p}^g$	specific heat capacity in constant pressure for specie i in the phase phase.	$\left[ \frac{J}{mol K} \right]$
$\tilde{H}^v$	specific molar enthalpy of vaporization.	$\left[ \frac{J}{mol} \right]$
$\Delta H$ ,	heat of reaction	$\left[ \frac{J}{s} \right]$
$I$	ionic strength	$\left[ \frac{mol}{l} \right]$
$K_G$	overall mass transfer coefficient	
$N$	mass transfer	$\left[ \frac{mol}{m^2 s} \right]$
$P^g$	partial pressure in the gas phase	[kPa]
$P^{g,eq}$	equilibrium partial pressure	
$R$	universal gas constant	$\left[ \frac{m^3 kPa}{K mol} \right]$
$T^g$	gas phase temperature	[K]
$T^l$	liquid phase temperature	[K]
$z$	leight of the control volume	[m]
$\zeta_A$	salting-out effect correction	

## References

- [1] IPCC, *Climate Change 2007: Synthesis report*, <http://www.ipcc.ch/ipccreports/index.htm>.
- [2] The free encyclopedia Wikipedia, *The greenhouse gases*, [http://en.wikipedia.org/wiki/Greenhouse\\_gas](http://en.wikipedia.org/wiki/Greenhouse_gas).
- [3] IPCC, *IPCC Special Report on Carbon dioxide capture and storage*, Cambridge university press, 2005.
- [4] Prakash D. Vaidya, Eugeny Y. Kenig, *CO<sub>2</sub>-alkanolamine reaction kinetics: a review of recent studies*, Chem. Eng. Technol., Vol. 30, No. 11, pp. 1467–1474, 2007.
- [5] Kohl Arthur, Nielsen Richard, *Gas Purification*, 5th edition, Gulf Publishing Company, 1997.
- [6] Mohamed Edali, Ahmed Aboudheir, Raphael Idem, *Kinetics of Carbon Dioxide Absorption into Mixed Aqueous Solutions of MDEA and MEA using Laminar Jet Apparatus and Numerically Solved Absorption-Rate/Kinetic Model*, Excerpt from the Proceedings of the COMSOL Conference 2007, Boston.
- [7] A. Aboudheir, P. Tontiwachwuthikula, A. Chakmab, R. Idema, *Kinetics of the reactive absorption of carbon dioxide in high CO<sub>2</sub>-loaded, concentrated aqueous monoethanolamine solutions*, Chem. Eng. Science, Vol. 58, pp. 5195–5210, 2003.
- [8] Yunda Liu, Luzheng Zhang, and Suphat Watanasiri, *Representing vapor-liquid equilibrium for an aqueous MEA-CO<sub>2</sub> system using the Electrolyte Nonrandom-Two-Liquid Model*, Ind. Eng. Chem. Res., Vol. 38, pp. 2080-2090, 1999.
- [9] Stefano Freguia and Gary T. Rochelle, *Modeling of CO<sub>2</sub> Capture by Aqueous Monoethanolamine*, AIChE Journal, Vol. 49, No. 7, 2003.
- [10] Karl A. Hoff, *Modeling and experimental study of carbon dioxide absorption in a membrane contactor*, Doctoral thesis, NTNU, 2003.
- [11] Eirik F. da Silva, Hallvard F. Svendsen, *Computational chemistry study of reactions, equilibrium and kinetics of chemical CO<sub>2</sub> absorption*, International journal of greenhouse gas control, Vol. I, pp. 151–157, 2007.
- [12] B. P. Mandal, M. Guhab, A. K. Biswas, S. S. Bandyopadhyaya, *Removal of carbon dioxide by absorption in mixed amines: modelling of absorption in aqueous MDEA-MEA and AMP-MEA solutions*, Chemical Engineering Science Vol. 56, pp. 6217–6224, 2001.
- [13] A. Benamor, M.K. Aroua, *Modeling of CO<sub>2</sub> solubility and carbamate concentration in DEA, MDEA and their mixtures using the Deshmukh-Mather model*, Fluid Phase Equilibria 231, pp. 150–162, 2005.
- [14] Daniel P. Hagewiesche, Sami S. Ashour, Hani A. Al-Ghawas, Orville C. Sandall, *Absorption of carbon dioxide into aqueous blends of monoethanolamine and -methyldiethanolamine*, Chemical Engineering Science, Vol. 50, No. 7, pp. 1071-1079, 1995.
- [15] R. Billet, *Packed Towers*, VCH Verlagsgesellschaft mbH, 1995.
- [16] R.C. Reid, J.M. Prausnitz, Bruce E. Poling, *The Properties of Gases and Liquids*, 4<sup>th</sup> edition, McGraw-Hill Inc., 1987.
- [17] E.D. Snijder, G.F. Versteeg, W.P.M. van Swaij, *Diffusion coefficients of several aqueous alkonolamine solutions*, J. Chem. Eng. Data, Vol. 38, pp. 475-480, 1993.
- [18] Jimmy Xiao, Chih-Wei Li, Meng-Hui Li, *Kinetics of absorption of carbon dioxide into*

- aqueous solutions of 2-amino-2-methyl-1-propanol+monoethanolamine*, Chemical Engineering Science, Vol. 55, pp. 161-175, 2000.
- [19] G.F. Versteeg, P.M.M. Blauwhoff, W.P.M. van Swaaij, *The effect of diffusivity on gas-liquid mass transfer in stirred vessels. Experiments at atmospheric and elevated pressures*, Chemical Engineering Science, Vol. 42, pp. 1103-1119, 1987.
- [20] A. Aroonwilas, A. Chakma, P. Tontiwaxhwuthikul, A. Veawab, *Mathematical modeling of mass-transfer and hydrodynamics in CO<sub>2</sub> absorbers packed with structured packings*, Chem. Eng. Science, Vol. 58, pp. 4037-4053, 2003.
- [21] Dag-Kjetil Hansen, *Dynamic modeling of an absorption tower for the removal of carbon dioxide from exhaust gas by means of monoethanolamine*, M.Sc. thesis, Telemark University College, 2004.