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## Rate-based Modelling and Validation of a Pilot Absorber Using MDEA Enhanced with Carbonic Anhydrase (CA)

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### Abstract

The great paradox of the 21st century is that we must meet the increasing global demand for energy and products while simultaneously mitigating the climate change. If both these criteria are to be met, carbon capture and storage is an imperative technology for sustainable energy infrastructure development. Post-combustion capture is a mature capture technology, however, to make it economically attractive, design of innovative solvents and process optimization is of crucial importance. An example for promising solvent is MDEA enhanced with carbonic anhydrase (CA), due to its fast kinetics and low solvent-regeneration energy demand.

The focus of this work is to develop a rate-based model for CO<sub>2</sub> absorption using MDEA enhanced with CA and to validate it against pilot-scale absorption experiments. In this work, we compare model predictions to measured temperature and CO<sub>2</sub> concentration profiles for different L/G ratios, lean CO<sub>2</sub> loadings, gas CO<sub>2</sub> content and packing height. We show that the developed model is suitable for CO<sub>2</sub> capture simulation and optimization using MDEA and MDEA enhanced with CA. Furthermore, we investigate the accuracy of the General Method (GM) enhancement factor model for CO<sub>2</sub> absorption/desorption using wetted-wall column data: 0 to 0.5 CO<sub>2</sub> loading and temperatures between 298 and 328 K. The present study represents a first step towards developing and optimizing a CA promoted MDEA CO<sub>2</sub> capture process.

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**Keywords:** CO<sub>2</sub> post-combustion capture; GM enhancement factor; Enzyme kinetics; Multiple reversible reactions; Model validation;

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## 1. Introduction

Reducing the carbon footprint of coal-fired power plants and subsequently mitigating the anthropogenic CO<sub>2</sub> emission rate is essential to stabilize the climate. On a global level, not one but the combination of different technologies is needed to reach this goal. One of these is post-combustion capture.

Aqueous amine based reactive absorption is the state-of-the-art technology for CO<sub>2</sub> post-combustion capture. In the last decades, several studies demonstrated that primary and secondary amines present a great potential for industrial scale CO<sub>2</sub> capture. The use of primary and secondary amines as absorbents rely on fast reaction with CO<sub>2</sub> compared to tertiary amines. However, an advantage of tertiary amines is their significantly lower regeneration energy demand relative to primary and secondary amines. Primary and secondary amines require smaller absorption towers while tertiary amines assure lower stripping energy demand. For this reason, various blends of primary/secondary amines and tertiary amines were proposed during the recent years. This combines the benefits of each amine: fast reaction and lower heat of desorption. An example is the blend of MDEA and MEA or MDEA and PZ. In these blends, MEA respectively PZ do not act only as promoter but they form stable carbamates; thus they significantly increase the regeneration energy requirement of the blend compared to MDEA.

A newly emerging alternative for CO<sub>2</sub> post-combustion capture is the use of biocatalyst (enzyme) to increase the CO<sub>2</sub> absorption rate. Enzymes promoted tertiary amines appear to be the ideal solution for CO<sub>2</sub> capture. These solvents have the potential for fast absorption and low regeneration energy. Enzymes are non-volatile and biodegradable catalysts. Carbonic anhydrases (CA) in particular are the most promising class of enzymes for improving reactive CO<sub>2</sub> absorption. They are considered to be the fastest and most selective biocatalyst known for the hydration of CO<sub>2</sub> [1]. Enzymes act as real biocatalyst assuring fast CO<sub>2</sub> absorption (smaller absorption tower) and they preserve the low heat of tertiary amines stripping.

Fosbøl et al. [2] showed that modeling principles are relatively well established and demonstrated using the benchmark MEA solvent, but only a few models and simulation studies exist for novel solvents and promoted systems. General rate-based models with accurate mass transfer and kinetic models, applicable to single and promoted solvents in a wide range of operating conditions should be developed and thoroughly validated. Only benchmarked models should be used to compare the absorption capacity and energy performance of solvents, to assess technical and economic feasibility, to study process alternatives and to optimize the operating conditions.

This paper presents a rate-based model for CO<sub>2</sub> absorption and desorption using MDEA and MDEA enhanced with CA. The developed model uses the extended UNIQUAC thermodynamic model [3] which is able to accurately predict vapor-liquid equilibrium (VLE) in the CO<sub>2</sub>-MDEA-H<sub>2</sub>O system. It also uses the GM enhancement factor model for reliable mass transfer rate calculation. The mass transfer area, hold-up and mass transfer resistance are calculated with the Billet and Schultes model [4]. The physical property correlations originate from literature.

Here, we validate this model against pilot-scale absorption experiments using MDEA and MDEA enhanced with CA solvents. These experiments were performed at Technical University of Denmark using a 10 m high absorption column equipped with Mellapak 250Y structured packing. Additionally, we compare the GM enhancement factor model against wetted-wall column data using MDEA and MDEA enhanced with CA (CA/MDEA): 0 – 50 wt.% MDEA with 0 to 1 wt.% CA; 0 to 0.4 mol/mol CO<sub>2</sub> loading and temperatures between 298 K and 328 K. We consider two parallel reactions: 1. the reaction between CO<sub>2</sub> and MDEA 2. the reversible CA catalyzed reaction between CO<sub>2</sub> and water, forming bicarbonate.

## 2. Simultaneous mass transfer and reaction modeling

This section presents the General Method (GM) enhancement factor model applied to MDEA and CA enhanced MDEA (CA/MDEA). First, it shows the applied reaction kinetics based on multiple second order reversible reactions and the Michaelis-Menten mechanism for the enzymatic effect. Then, it briefly presents the equations of the GM model for parallel reactions. This model uses off-the-shell correlations for physical properties in combination with the extended UNIQUAC thermodynamic model [5].

## 2.1. Reaction Kinetics

The reaction kinetics of CO<sub>2</sub> with MDEA respectively CA/MDEA consists of several parallel reactions. Implementation of such a mechanism in a mass transfer model is a laborious task and it results in significant increase of the computational time. To reduce the complexity of the model we apply a simplified kinetics based [6–8]. In this work, we account for the reaction between MDEA and CO<sub>2</sub>, reaction (1) respectively the enzyme promoted hydration reaction of CO<sub>2</sub>, reaction (2). Thus, this model applies to systems with and without enzyme.



The reaction between CO<sub>2</sub> and MDEA, reaction (1) is overall second order and it is first order with respect to the reactants, i.e. CO<sub>2</sub> and MDEA [6]. The change in the concentration of H<sub>2</sub>O is negligible as its concentration is much greater than the concentration of CO<sub>2</sub> and MDEA. Based on these assumptions, the kinetic rate expression is:

$$R_{\text{MDEA}} = k_{\text{MDEA}} C_{\text{MDEA}} C_{\text{CO}_2} \quad (3)$$

where the reaction rate constant,  $k_{\text{MDEA}}$  originates from Versteeg et al. (1996):

$$k_{\text{MDEA}} = 3.82 \cdot 10^5 \cdot \exp\left(-\frac{5080}{T(K)}\right) \frac{\text{mol}}{\text{m}^3 \text{s}} \quad (4)$$

Penders-van Elk showed that CA accelerates the formation of bicarbonate ion and the release of a proton by converting water to active hydroxyl ion. Essentially, CA enhances the reaction of carbon dioxide with water and it does not enhance the reaction of CO<sub>2</sub> with MDEA [7]. Accordingly, the complex mechanism of enzyme catalyzed CO<sub>2</sub> absorption practically reduces to reaction (2). In this work, the reaction rate of carbonic anhydrase catalyzed CO<sub>2</sub> hydration reaction, reaction (2) is given by Michaelis-Menten kinetics:

$$R_{\text{H}_2\text{O:CA}} = \frac{k_{\text{cat}}}{K_M + C_{\text{CO}_2}} C_{\text{CA}} C_{\text{CO}_2} C_{\text{H}_2\text{O}} \quad (5)$$

where the Michaelis-Menten constant  $K_M$  (mol·m<sup>-3</sup>) shows the CO<sub>2</sub> concentration,  $C_{\text{CO}_2}$ , (mol·m<sup>-3</sup>) at which the enzyme reaction rate is halved.  $k_{\text{cat}}$  is the so-called turnover number and  $C_{\text{CA}}$  is the concentration of the enzyme (mol·m<sup>-3</sup>). Since the CO<sub>2</sub> concentration is usually very low at absorption conditions compared to the Michaelis Menten constant [7,10]. Equation (5) further simplifies using a  $k_{\text{enz}}$  (m<sup>3</sup>·mol<sup>-1</sup>·s<sup>-1</sup>) instead of the Michaelis Menten description. This simplification leads to:

$$R_{\text{H}_2\text{O:CA}} = k_{\text{enz}} C_{\text{CA}} C_{\text{CO}_2} C_{\text{H}_2\text{O}} = k_{\text{enz}}^{\text{app}} C_{\text{CO}_2} C_{\text{H}_2\text{O}} \quad (6)$$

Based on the work of Gladis et al. [10], in this work we use the expression (7) which consists of the simplified Michaelis-Menten model combined with a bicarbonate product inhibition term, as the reaction rate showed a decline when experiments were performed at higher loadings for the enzyme reaction rate constant.

$$k_{\text{enz}}^{\text{app}} = \frac{k_{\text{CA},1}}{1 + \frac{C_{\text{HCO}_3^-}}{k_{\text{CA},2}}} C_{\text{CA}} \quad (7)$$

where  $k_{CA,1}$  respectively  $k_{CA,2}$  are temperature dependent adjustable parameters and the term  $k_{HCO_3}/k_{CA,2}$  accounts for the enzyme inhibition by the bicarbonate ion. This kinetics with two reactions is used with the GM model to calculate the  $CO_2$  absorption and desorption rate.

## 2.2. Mass transfer rate enhancement

This section presents the equation system to calculate the enhancement of the mass transfer rate by reactions (1) and (2). The model is set up assuming that only thermodynamic interaction exists between the two reactions and the acceleration of the mass transfer rate due to each reaction is distributed per equilibria. The coupling between the individual reactions is through the underlying thermodynamic model providing the bulk compositions of the reactants and products. In other words, the overall mass transfer intensification ( $E_{overall}$ ) is the combined effect of the individual reactions (1) and (2):

$$E_{overall} = E_{R_{MDEA}} + E_{R_{H_2O:CA}} - 1 \quad (8)$$

where  $E_{R_{MDEA}}$  and  $E_{R_{H_2O:CA}}$  are the enhancement factors for reactions (1) and (2). These are reversible reactions where 1 mol of  $CO_2$  reacts with  $\nu_B$  moles of base  $B$  ( $B = MDEA:H_2O$  and  $H_2O:CA$ ). One can see in eq. (8) that for MDEA without enzyme,  $E_{R_{H_2O:CA}} = 1$ .

According to the GM model, the enhancement factor for the individual (single) reactions is the solution of the equations system (9) and (10).

$$E_{R_i} = Ha_{R_i} \sqrt{y_{B,R_i}^i} \frac{1 - y_{CO_2,R_i}^*}{1 - y_{CO_2}^b} \quad (9)$$

$$E_{R_i} = 1 + (E_{\infty,R_i}^* - 1) \frac{1 - y_{B,R_i}^i}{1 - y_{CO_2}^b} \quad (10)$$

where  $E_{R_i}$  is the enhancement factor of the  $R_i$ -th individual reaction:  $E_{R_i} = E_{R_{MDEA}}$  respectively  $E_{R_i} = E_{R_{H_2O:CA}}$  and  $B$  refers to  $MDEA$  respectively  $H_2O:CA$ . Equations (9) and (10) form a system of nonlinear equations with two unknowns,  $E_{R_i}$  and  $y_{B,R_i}^i$ . Eliminating  $E_{R_i}$  leads to a single algebraic equation in  $y_{B,R_i}^i$  which can be solved using methods such as the secant method, the Broyden method, the Newton method, etc. The solution methodology is presented in [12].

The Hatta number ( $Ha_{R_i}$ ) and instantaneous enhancement factor ( $E_{\infty,R_i}^*$ ) in equations (9) and (10) are:

$$Ha_{R_i} = \frac{\sqrt{k_{R_i} C_B^b D_{CO_2}}}{k_L} \quad (11)$$

$$E_{\infty,R_i}^* = 1 + \frac{D_B C_B^b}{\nu_B D_{CO_2} C_{CO_2}^i} \quad (12)$$

$D_B$  and  $D_{CO_2}$  are the diffusion coefficients of  $B$  respectively  $CO_2$ .  $C_B^b$  and  $C_{CO_2}^i$  denote the concentration of the base in the liquid bulk respectively the concentration of  $CO_2$  at the gas-liquid interphase; the dimensionless parameter

$y_{CO_2}^b = C_{CO_2}^b / C_{CO_2}^i$  is given by the extended UNIQUAC thermodynamic model. The  $CO_2$  concentration that would be in equilibrium with the interface concentration is:

$$y_{CO_2, R_i}^* = y_{CO_2, b} \frac{y_{P_1, R_i} y_{P_2, R_i}}{y_{B, R_i}^{v_B}} \tag{13}$$

where  $P_1$  and  $P_2$  refer to reaction products and  $B$  is MDEA respectively  $H_2O:CA$ .  $y_{P_1, R_i}^i$  and  $y_{P_2, R_i}^i$  are given by:

$$y_{P_j, R_i}^i = 1 + \frac{D_B C_B^b}{v_B D_{P_j} C_{P_j}^b} (1 - y_{B, R_i}^i) \tag{14}$$

where  $j=1$  and  $2$ . Note, the stoichiometric coefficient of  $B$ ,  $v_B$  is  $1$  for reaction (1) and it is  $2$  for reaction (2).

The overall enhancement factor,  $E_{overall}$  is needed to determine the  $CO_2$  mass transfer flux across the gas-liquid interface,  $J_{CO_2, gl}$  according to:

$$J_{CO_2, gl} \approx \frac{1}{1/k_{CO_2}^g + H_{CO_2} / E_{overall} k_{CO_2}^l} (p_{CO_2} - p_{CO_2}^*) \tag{15}$$

$k_{CO_2}^g$  and  $k_{CO_2}^l$  are the partial mass transfer coefficients for the gas side and for the liquid side and  $H_{CO_2}$  is the Henry constant. The driving force for mass transfer is the difference between the partial pressure of  $CO_2$  in the gas phase,  $p_{CO_2}$  and the equilibrium partial pressure of  $CO_2$  exerted from the liquid phase,  $p_{CO_2}^*$ . The gas side and liquid side mass transfer coefficients for the wetted wall column at Technical University of Denmark was determined experimentally by Gladis et al. [11].

### 3. Rate-based model for MDEA enhanced CA

The steady-state rate-based model for  $CO_2$  absorption applied to MDEA and CA/MDEA is based on the equation system proposed by Gabrielsen [13]. This model consists of flow and transport equations describing the flow rate, composition and temperature of the gas phase respectively of the liquid phase. It is formulated as a boundary value problem (BVP) with fixed inlet conditions. The gas stream composition, temperature and molar flow are specified at the bottom while the liquid stream characteristics are specified at the top of the column. These conservation equations, a system of ordinary differential equations, are coupled with non-linear algebraic equations providing the mass transfer and the hydraulic parameters [4], e.g. partial mass transfer coefficients, hold-up, effective mass transfer area and pressure drop. The model uses the extended UNIQUAC thermodynamic model for vapor-liquid equilibria (VLE) and thermal properties calculation [3,5]. The above presented General Model (GM) enhancement factor model describes the acceleration of mass transfer rate due to the reaction between a base and  $CO_2$ . Temperature and composition dependent correlations for physical properties such as viscosity, diffusivity, surface tension and density originate from the open-literature[14].

## 4. Results and discussions

### 4.1. Mass transfer model validation

This section shows the validation of the GM model against wetted-wall column experimental data for MDEA and enzyme enhanced MDEA (CA/MDEA). The GM predictions are compared against a large number of experimental

data covering a broad range of CO<sub>2</sub> loadings, between 0 and 0.54 mol CO<sub>2</sub>/mol MDEA, at temperatures of 25°C, 40°C and 55°C, for both absorption and desorption of CO<sub>2</sub>. These experiments were carried out at different MDEA respectively enzyme concentrations. Table 1 gives an overview of the experimental conditions for the wetted wall column measurements [11]. These experimental data were screened for outliers. First, the measurements corresponding to the lowest partial pressure were eliminated due to very low the CO<sub>2</sub> concentration, i.e. near the detection limit of the concentration probe. Furthermore, the measured CO<sub>2</sub> flux was represented versus the driving force. Generally, the dependency between mass transfer flux and driving force is linear since the experiments were carried out near the pseudo-first order reaction regime. Thus, the points greatly deviating from this line are most probably outliers and they were eliminated. Note that the points deviating from the linear trend presented relative absolute deviations above 100% from the GM calculated values.

Table 1. Input specifications for the wetted-wall column measurements

Parameter	Unit	MDEA	CA enhanced MDEA
Number of experimental data		80	256
Amine concentration	mol/kg water	4	1, 4, 8
Amine concentration	wt.%	30	15, 30, 55
Enzyme (CA) concentration	mol/m <sup>3</sup>	0	0.05, 0.1
CO <sub>2</sub> loading	mol/mol	0 – 0.53	0 – 0.54
Temperature	°C	25, 40, 55	25, 40, 55
Driving force	kPa	-93 – 33	-45 – 30
CO <sub>2</sub> molar flux	mol/m <sup>2</sup> s	-0.003 – 0.003	-0.01 – 0.01

Fig.1 show the calculated CO<sub>2</sub> flux as function of measured values using MDEA at different CO<sub>2</sub> loadings. This figure underlines that the relative deviations are generally within  $\pm 25\%$ , indifferent of loading. The mean absolute relative deviation (MARD) is 20.1%. Fig.1 shows that only a few points at 0.03 CO<sub>2</sub> loading are visibly outside of the  $\pm 25\%$  accuracy range when the model under-predicts the measured values. A possible explanation is the high susceptibility of CO<sub>2</sub> towards very lean MDEA solution, which may result in additional dissolution of CO<sub>2</sub> from air during sampling and analysis. This leads to under-predicted CO<sub>2</sub> flux. Note that unloaded and very lean solutions are not relevant for the CO<sub>2</sub> capture business.

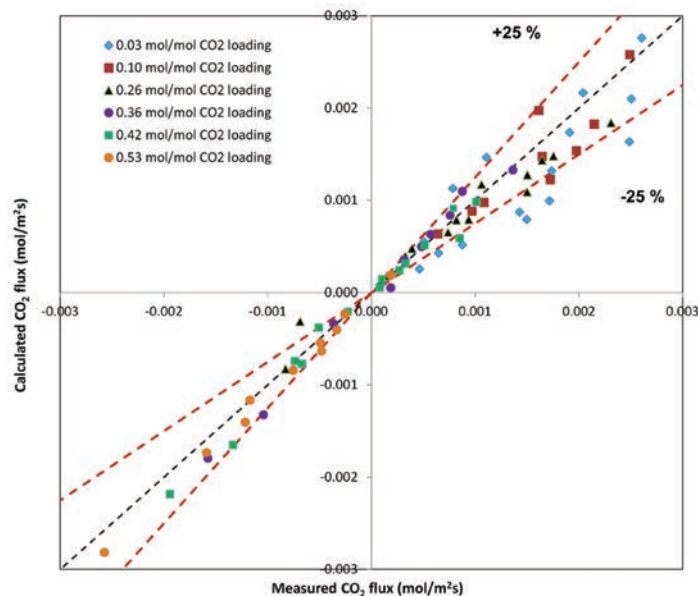
Fig.1. Predicted versus measured CO<sub>2</sub> flux for 30 wt.% MDEA solution at different CO<sub>2</sub> loadings

Fig.2 illustrates the fit between the model and experiment for 30 wt.% MDEA + 0.1% CA solution at different CO<sub>2</sub> loadings. The agreement between the model and experiment is good. Some of the data are a bit under- and some of the data are a bit over-predicted by the model. Only a few point deviates noticeably from the mean at 0.03 and 0.54 CO<sub>2</sub> loadings, similar to the results for MDEA without enzyme in Fig.1. However, the error is not systematic with respect to loading.

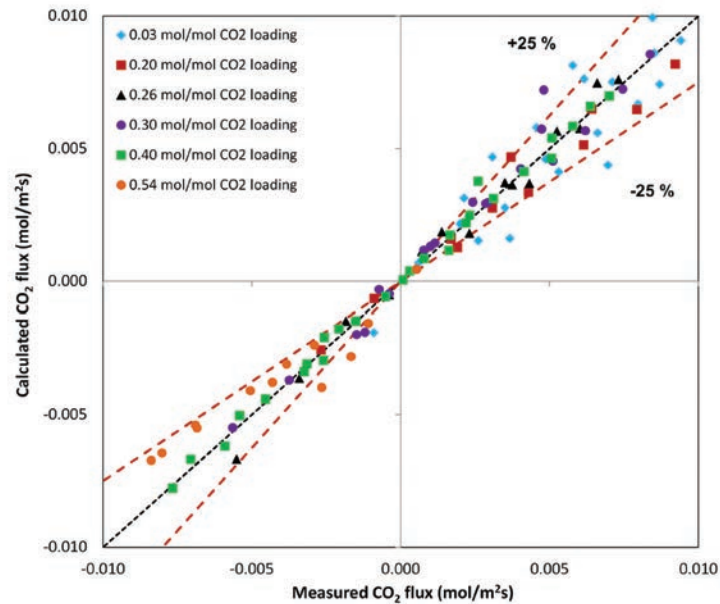


Fig.2. Predicted versus measured CO<sub>2</sub> flux using 30 wt.% MDEA + 0.1% CA at different loadings

Fig. 3 shows the ratio of the GM calculated and experimental overall mass transfer coefficient as function of the importance of the main/dominant reaction (2). It shows the results for MDEA enhanced with CA at different concentrations. For comparison purposes, this figure also shows the GM model versus 30 wt.% MEA experimental data from Dugas [15]. In this figure, the importance of the main/dominant reaction is the ratio of the enhancement factor for reaction (2) compared to the overall enhancement factor. Therefore, this parameter indicates the relevance of the mass transfer rate acceleration by the two participating reactions. For MEA, this parameter is 100% as we assume that CO<sub>2</sub> reacts with MEA according to one single second order reversible reaction [12]. For CA/MDEA, this parameter is between 65% and 95%, showing that it is important to account for both of the reactions when predicting the CO<sub>2</sub> absorption/desorption rate in CA/MDEA. Note that Gaspar et al. [12] demonstrated that GM model practically reduces to the two-film model for MEA. Therefore, the MEA comparison acts as a reference for the expected accuracy when comparing GM to wetted-wall data.

Fig. 3 shows that the accuracy of the GM model is comparable between MEA and CA/MDEA. The deviations between model and experiment are up to 25% for both of the solutions. Thus, GM is suitable for mass transfer prediction using CA/MDEA. Furthermore, this figure shows that the importance of the reaction between CO<sub>2</sub> and MDEA is greater at higher MDEA concentrations, as expected. The importance of the main reaction is between 65% and 85% for 50% MDEA + 0.05%CA, it is between 75% and 95% for 30% MDEA + 0.05% CA and it is between 85% and 95% for the 15% MDEA + 0.05%CA solution.



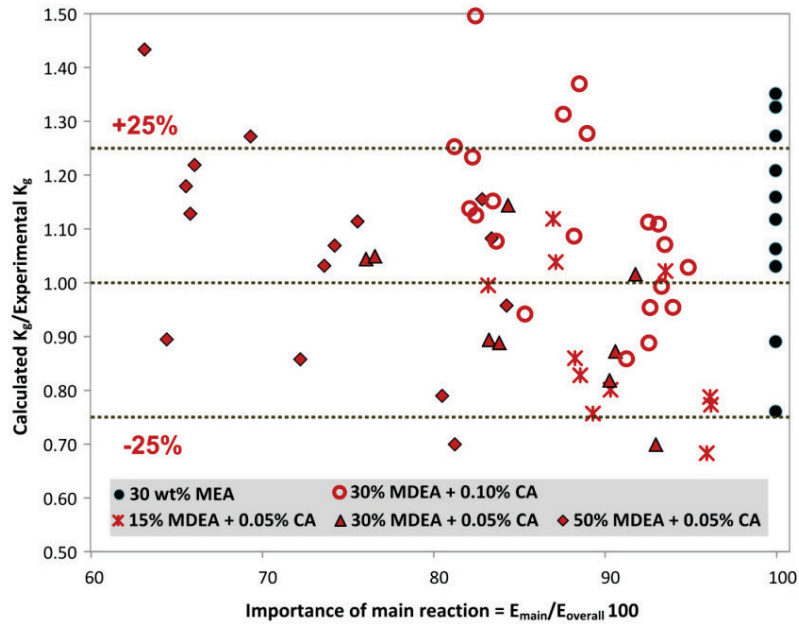


Fig. 3. Ratio of calculated and measured overall mass transfer coefficient as function of importance of reaction 2 for MEA and CA/MDEA

Based on these findings, it can be concluded that the simplified Michaelis Menten kinetics represents adequately the CA enhanced MDEA system in the investigated enzyme and  $\text{CO}_2$  concentration range. The agreement between the GM model and experiment is satisfactory ( $\pm 25\%$ ), without systematic deviations with respect to importance of reaction (2), loading, MDEA concentration or enzyme concentration.

#### 4.2. Rate-based absorber model validation

This section shows the validation of the rate-based model for  $\text{CO}_2$  absorption using MDEA and CA enhanced MDEA (CA/MDEA). Here, we show model and experimental  $\text{CO}_2$  loading and temperature profiles for two campaigns: (campaign 1) with MDEA and (campaign 2) with CA enhanced MDEA. Campaign 2 was divided in two sections: (campaign 2A) fixed packing height of 10 m and (campaign 2B) packing heights of 2, 4, 6, 8, and 10 m. Both of the campaigns were run with a synthetic flue gas, saturated at the absorber's inlet temperature. The synthetic saturated flue gas contained various  $\text{CO}_2$  percent's from 3.6% to 13.6%. The low  $\text{CO}_2$  content (3.6 – 5.3%  $\text{CO}_2$ ) resembles a flue gas from a natural gas combined cycle power plant (NGCC) and the high  $\text{CO}_2$  concentration (> 11%  $\text{CO}_2$ ) corresponds to a flue gas from a coal fired power plant. The MDEA concentration was 30 wt.% for these campaigns and the CA/MDEA campaign was run with 0.05 mol/m<sup>3</sup> CA. These campaigns covered various liquid to gas (L/G) ratios and different inlet lean  $\text{CO}_2$  loadings. Campaign 1 was run with fresh MDEA solvent and its inlet lean loading was between 0.01 and 0.09 mol/mol. Most of the experiments in campaign 2 were performed with a loaded solution of 0.2 – 0.25 mol  $\text{CO}_2$ /mol MDEA. Table 2 summarizes the main design specifications and operating conditions. Further details regarding the experimental setup and analysis can be found in [16,17].

Table 2. Main operating conditions and column specifications for MDEA

Column specifications		
Absorber packing height (m)	2 – 10	
Absorber diameter (m)	0.1	
Packing type	Mellapak 250Y	
Operating conditions	Campaign 1	Campaign 2
Flue gas flow rate (kg/h)	30	30
L/G ratio (kg/kg)	2.4 – 6.6	2.3 – 5.9
Inlet CO <sub>2</sub> mol %	4.3 – 13.1	3.6 – 13.5
MDEA concentration (wt.%)	30	30
CA concentration (mol/m <sup>3</sup> )	-	0.05
Lean CO <sub>2</sub> loading (mol/mol)	0.01 – 0.09	0.19 – 0.34
Gas temperature (°C)	25 – 30	25 – 30
Lean temperature (°C)	30 – 43	25 – 42

Fig. 4 shows the calculated versus measured rich CO<sub>2</sub> loading for campaigns 1 and 2. This figure illustrates that generally the agreement between model and experiment is good with both solvents (MDEA and CA/MDEA) nevertheless of the flue gas CO<sub>2</sub> concentration. Campaign 2B, performed with packing heights of 2, 4, 6, 8 and 10 m is a little over-predicted by the model. In campaign 2B, two tests were performed for each height with constant flue gas flow rate and L/G ratios of 2.4 kg/kg and 5.6 kg/kg. The analysis revealed that the error is not systematic neither with respect to packing height nor L/G ratio; thus the model describes fairly well the effect of height on CO<sub>2</sub> absorption.

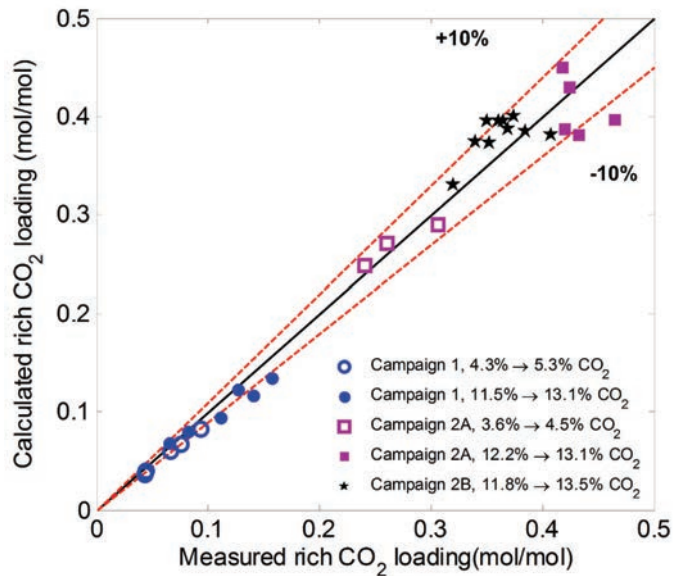


Fig.4. Calculated versus measured rich CO<sub>2</sub> loading using MDEA (campaign 1) and CA/MDEA (campaign 2)

The performance of the model is further illustrated in fig. 5. This figure shows the variation of CO<sub>2</sub> loading versus the column height using MDEA and CA/MDEA. It outlines that the model and experiments almost overlap

for flue gas CO<sub>2</sub> concentrations of 3.6% to 5% and the model is less accurate at high CO<sub>2</sub> concentration, especially for CA/MDEA solvent. This behavior may be related to the bicarbonate inhibition of the enzymatic effect, eq. (7). Note that the bicarbonate concentration decreases from bottom to top, proportional to CO<sub>2</sub> loading. An offset in this inhibition factor results in an offset in the calculated reaction rate and therefore it leads to an offset in CO<sub>2</sub> absorption rate respectively CO<sub>2</sub> loading. The simplified reaction mechanism, the kinetic parameters and the enhancement factor model strongly influences the shape of the concentration and temperature profiles, as shown in the benchmarking analysis using MEA [2].

Furthermore, the discrepancy between the model and experiment in fig. 5 could be related to the hydraulic and mass transfer models. The benchmarking study on MEA [2] showed that the mass transfer correlation significantly influences the concentrations and temperatures along the column height. Similar conclusion was reached by [18,19]. They showed that the choice of model used to describe the liquid hold-up in the column exerts a significant influence on the mass transfer area and the mass transfer coefficients. Therefore, accurate prediction of the mid-section may require additional adjustment of the mass transfer model, reaction kinetics and re-evaluation of assumptions, e.g. liquid film reaction, equilibrium assumption at the interface, negligible heat loss to the surrounding, etc.

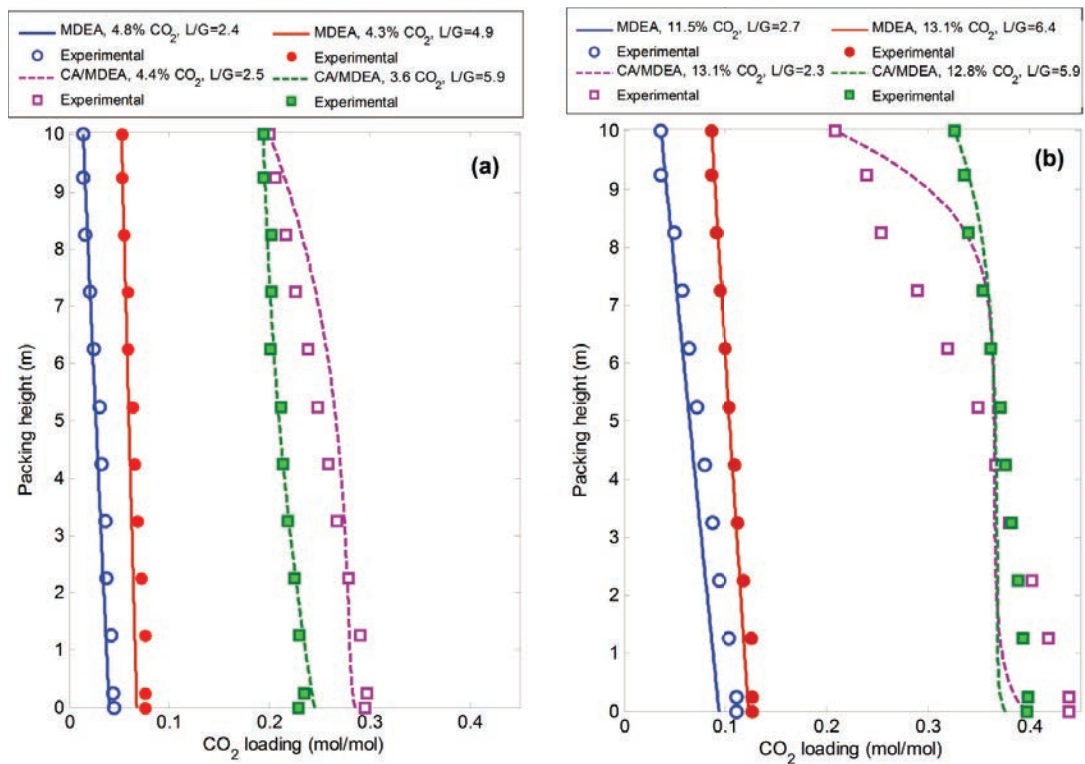


Fig. 5. Measured and calculated CO<sub>2</sub> loading versus height using MDEA and CA/MDEA at (a) low flue gas CO<sub>2</sub> concentrations and (b) high flue gas CO<sub>2</sub> concentrations.

Based on figures 4 and 5, it can be concluded that the model generally predicts well the CO<sub>2</sub> absorption using MDEA respectively CA enhanced MDEA. The relative deviations between calculated and measured lean outlet loadings are within  $\pm 10\%$  for CO<sub>2</sub> flue gas concentrations of 3.6% to 13.5% and for low and high L/G ratios.

## 5. Conclusions

This work presented a simple but reliable mass transfer calculation approach for CO<sub>2</sub> absorption and desorption and extended the DTU-CAPCO<sub>2</sub> rate-based model for absorption simulation using MDEA and carbonic anhydrase (CA) enhanced MDEA. The validation of these models is also presented in here.

The implemented mass transfer (GM) model includes two parallel reactions: (1) the reaction between CO<sub>2</sub> and MDEA and (2) the CA catalyzed CO<sub>2</sub> hydration reaction. The distribution of CO<sub>2</sub> reaction rates between the two reactions is as function of their equilibrium constant. This GM enhancement factor model has been compared to a large number of wetted-wall column measurements for both, CO<sub>2</sub> absorption and desorption. The results showed that GM predicts the wetted-wall data within an accuracy of  $\pm 25\%$  with a mean absolute relative deviation (MARD) of 20.1% for MDEA respectively 18.5% for CA enhanced MDEA systems. Moreover, this study showed that the simplified Michaelis Menten expression (7) with  $k_{CA,1}$  and  $k_{CA,2}$  adjustable kinetic parameters accurately predicts the CO<sub>2</sub> mass transfer rate using CA enhanced MDEA as solvent. This model uses off-the-shell correlations for physical properties in combination with the extended UNIQUAC thermodynamic model.

A rate based model for CO<sub>2</sub> absorption using MDEA enzyme promoted MDEA (CA/MDEA) has been developed and validated against experimental data. This model applies the General Model (GM) enhancement factor model to determine the CO<sub>2</sub> mass transfer rate across the gas-liquid interface in combination with the extended UNIQUAC thermodynamic model and the Billet and Schultes model mass transfer and hydraulic correlation. It also uses temperature and concentration dependent correlations for physical properties. The results showed that the agreement between the rate-based model predictions and experimental pilot absorber measurements is good. The relative deviations between simulated and measured CO<sub>2</sub> capture percentage, lean loading are generally within  $\pm 10\%$ . Also the agreement between experimental and simulated CO<sub>2</sub> concentration and temperature profiles through the column is good, in the expected range of variability of error [2].

The developed model is a useful tool for simulation of CO<sub>2</sub> absorption in CA/MDEA. It can be used to simulate flue gas cleaning of natural gas combined cycle and coal based power plants. However, awareness must be taken when using any model for column scale-up/design. These simulations showed that for some cases the model deviates from the measured composition and temperature profiles. This could lead to over- or under-predicted height required to capture a specified amount of CO<sub>2</sub>. It is recommended to investigate the sensitivity of the composition and temperature profiles with respect to mass transfer, hydraulic, thermodynamic and kinetic sub-models for a wide range of operating conditions in order to increase confidence in model-based design.

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