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## Pilot absorption experiments with carbonic anhydrase enhanced MDEA

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### Abstract

Mass transfer experiments were carried out on DTU's pilot absorber unit, a 10 m high column packed with 250 Y Mellapak structured packing. The influence of temperature, solvent loading, column height and liquid flowrates on absorption performance were determined for a 30 wt% N-methyl-diethanolamine (MDEA) solvent, with and without the enzyme carbonic anhydrase (CA). The absorption experiments were performed at atmospheric pressure and a gas phase carbon dioxide mole fraction of 0.13. During experiments liquid samples were withdrawn at each meter of column height and the solvent loading was determined by both a density method and the BaCl<sub>2</sub> method. After the solvent was loaded to equilibrium it was heated up and reintroduced into the column, where CO<sub>2</sub> was stripped off using air as stripping gas. The addition of CA increased the mass transfer significantly in all experiments. Lower absorption temperatures resulted in higher mass transfer in absorption, when 28 and 40 °C inlet temperature were chosen. The absorption performance decreased with lower solvent flow. The enzyme was also capable of enhancing the desorption process, where higher desorption rates were measured at 45 and 50 °C with CA enhanced solvent compared to 55 °C without CA.

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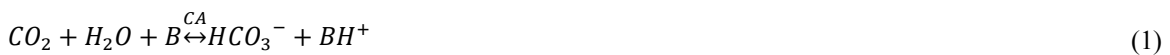
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*Keywords:* pilot plant, CCS, carbonic anhydrase, absorption, desorption

## 1. Introduction

Today's society is facing several issues: on the one hand a growing population requires an increased energy supply, while on the other hand greenhouse gas emissions need to be reduced to limit their effect on global warming. These two problems are however linked, since the majority of energy is generated by burning fossil fuel in power stations. Carbon capture and storage technology (CCS) can play a major role in the ambitious goals for greenhouse gas emission reduction while also ensuring a safe energy supply. The greenhouse gas CO<sub>2</sub> is captured at the point of generation and then stored beneath the surface and thus prevented from entering the atmosphere. The most mature technology in this field is a chemical absorption/desorption process which can also be retrofitted to existing power plants [1]. Here the flue gas is brought into contact with a liquid chemical solvent in an absorber unit. Carbon dioxide is selectively dissolved in the liquid phase where it undergoes a chemical reaction with the solvent. This reaction is a crucial part of this process since the depletion of CO<sub>2</sub> in the liquid creates a sharper concentration gradient and enhances the mass transfer. After the flue gas is cleaned and the solvent has reacted with CO<sub>2</sub> it is pumped into the desorber for regeneration. The chemical and thermodynamic equilibrium are shifted by the addition of thermal energy and pure CO<sub>2</sub> is recovered which now can be compressed and stored. A link between reaction speed and heat of reaction has been found for alkanolamines, the most prominent group of carbon capture solvents [2]. As the reactions need to be reversed in the desorber, the desorber unit needs more than 60% of the overall energy. For an economical process the capital costs, as well as the operational costs, have to be as low as possible, especially since there is no valuable product generated in this process. Therefore higher mass transfer in absorption, which is needed for low capital costs as smaller unit operations can be built, are offset by higher energy input for reversing the reactions in the desorber thus increasing the operational costs.

A possible way to circumvent this dependency is the use of kinetic promoters in combination with slow absorbing solvents with low heats of reaction [3]. One promising kinetic promoter is the enzyme carbonic anhydrase (CA) which catalyses the following reversible reaction:



Enzymes are true catalysts, so they do not change the thermodynamic equilibrium of the reaction [4]. They catalyse a certain reaction, if the reaction products are thermodynamically stable and are catalysing the reaction towards the chemical equilibrium. They can therefore act as a promoter for absorption and desorption. The mass transfer in a chemical absorption process can be described with the following equation as the ratio of driving force to resistance:

$$N_{CO_2} = \frac{(P_{CO_2}^{gas} - H_{CO_2} \cdot C_{CO_2}^{liq})}{\frac{1}{k_{CO_2}^{gas}} + \frac{H_{CO_2}}{k_{CO_2}^{liq} \cdot E}} a_{eff} \quad (2)$$

Where  $N_{CO_2}$  (mole s<sup>-1</sup>) is the flux of CO<sub>2</sub> through the interface,  $P_{CO_2}^{gas}$  (Pa) is the partial pressure of CO<sub>2</sub> in the gas phase,  $C_{CO_2}^{liq}$  (mole m<sup>-3</sup>) is the concentration of CO<sub>2</sub> in the liquid phase,  $H_{CO_2}$  (Pa m<sup>3</sup> mole<sup>-1</sup>) is the apparent Henry coefficient for CO<sub>2</sub> in the solvent; the product of  $H_{CO_2}$  and  $C_{CO_2}^{liq}$  is the equilibrium partial pressure of the solvent

$P_{CO_2}^{liq}$  (Pa). The mass transfer coefficient in the gas and the liquid phase are denoted as  $k_{CO_2}^{gas}$  (mole Pa<sup>-1</sup> m<sup>-2</sup> s<sup>-1</sup>) and  $k_{CO_2}^{liq0}$  (m s<sup>-1</sup>). The latter is the physical mass transfer coefficient in the absence of a chemical reaction, thus describing the mass transfer due to diffusion. The Enhancement factor E (-) accounts for the effect of reaction on the mass transfer, and is the ratio of mass transfer with chemical reactions to mass transfer purely due to diffusion. The mass transfer is also dependent on the mass transfer area  $a_{eff}$  (m<sup>2</sup>). The enzyme catalyzes the reaction between CO<sub>2</sub> and water, will therefore solely influence the Enhancement factor E in the mass transfer equation (Eq. (2)).

The feasibility of applying CA as a kinetic rate promoter in CO<sub>2</sub> absorption has been proven in lab scale in several studies [5], [6], but experimental data from larger scale operation is seldom reported in the open literature, especially data on how the process conditions influence the mass transfer .

Kunze and co-workers [7] performed pilot scale absorption experiments in a packed column with 30 wt% MDEA and 10 wt% K<sub>2</sub>CO<sub>3</sub> solutions at 317 K. They reported no undesired side effects, such as foaming or increased pressure drop and observed an increase in catalytic effect (absorbed mole flow of CO<sub>2</sub> with CA/ absorbed mole flow with solvent alone) with increased liquid load.

The aim of this study is to give a better insight into the enzyme enhanced CO<sub>2</sub> capture process by revealing the influence of absorption temperature, solvent lean loading and column height on the mass transfer of CO<sub>2</sub> at pilot scale. The effect of enzyme on desorption will be likewise investigated.

## 2. Materials and methods

### 2.1. Pilot scale setup

The unit operation used in this study is a packed column filled with Mellapak 250 Y structured packing. The total height of the column is 10 m, whereas the height of the filling elements is 8.2 m in total, equally distributed over the height of the column; each 1m of the column has 4 packing elements of 0.205 m, i.e. 0.82 m packing material per meter of column. The inner diameter of the column is 0.1 m, whereas the packing elements have a diameter of 0.084 m. Wall deflectors are connected to the packing elements, preventing the gas flow from bypassing the packing on the sides and redistributing the liquid from the walls of the column. The column has 5 liquid inlet points for every two meters of height. The liquid is pumped from large storage tanks or jacketed heating tanks. In case an elevated temperature is needed a heat exchanger is used that is supplied with heat from a domestic water heater connected with a pump in closed loop. The gas system in absorption experiments was in a closed cycle using a fan and adding only pure CO<sub>2</sub> to the system. Thus the gas is saturated with water and solvent vapor at the inlet temperature.

The entering mass flows of the gas and the liquid were recorded with a high performance Coriolis flowmeter from Endress+Hausser. At the gas inlet and gas outlet CO<sub>2</sub> volume concentration (NDIR-probe from Vaisala), pressure and temperature are also measured. The column temperature was measured over the whole height at each meter.

### 2.2. Experimental procedure

The solvent was mixed in storage tanks to the desired concentration and then pumped around bypassing the column for a proper mixing and heated when required. The column was flushed with pure N<sub>2</sub> for half an hour before the experiments were started in an open loop. The loop was then closed and pure nitrogen was circulated and CO<sub>2</sub> introduced to reach a mole fraction of 0.13. When the solvent was introduced into the column, CO<sub>2</sub> was added to reach a steady inlet concentration. After having 10 min of constant outlet CO<sub>2</sub> mole fraction, liquid samples were drawn from a sample valve at each meter of the column starting from the bottom to not disturb the liquid flow inside the column and change the absorption. The liquid sampling procedure was performed fast, never exceeding 5

minutes. Afterwards one process condition was changed, either column height or liquid flowrate and a new steady state was achieved. The liquid samples were analyzed in the lab: For the inlet and outlet samples a  $\text{BaCl}_2$  titration method was used [9] in combination with a density method, that was previously proven to work for a MEA solvent in our lab [10]. The liquid samples from the column heights were then analyzed with the density method using a density correlation provided by Weiland and co-workers [11], after calibration.

The liquid solvent was loaded inside the absorber to equilibrium for the desorption experiments, and was then heated up inside the column. Dry pressurized air was introduced into the column at the bottom and the  $\text{CO}_2$  was stripped off. The amount could be measured at the gas outlet, as well as by the liquid phase analysis. The experiments were performed with an open system; the exhaust gas was feed to the ventilation in these experiments. The amount of absorbed  $\text{CO}_2$  was calculated from the mole balance over the gas phase.

### 2.3. Experimental setpoints

The aim of these experiments was to determine the absorption of  $\text{CO}_2$  into enzyme enhanced solvents, a process that is limited by the reaction kinetics between the solvent and carbon dioxide in the liquid phase. Therefore the gas flowrate was not varied throughout the experiments, but was kept constant at a gas capacity factor of about  $0.98 \text{ Pa}^{0.5}$ , a rather high value. For this reason not all of the  $\text{CO}_2$  could be absorbed inside the column, but it generated higher mass transfer rates, which resulted in higher changes in the solvent loading over the column height.

## 3. Experimental results

Experiments were performed to determine the effect of column height on absorption and desorption. Furthermore the effect of liquid flow rate, liquid temperature and solvent loading was investigated

### 3.1. Absorption height

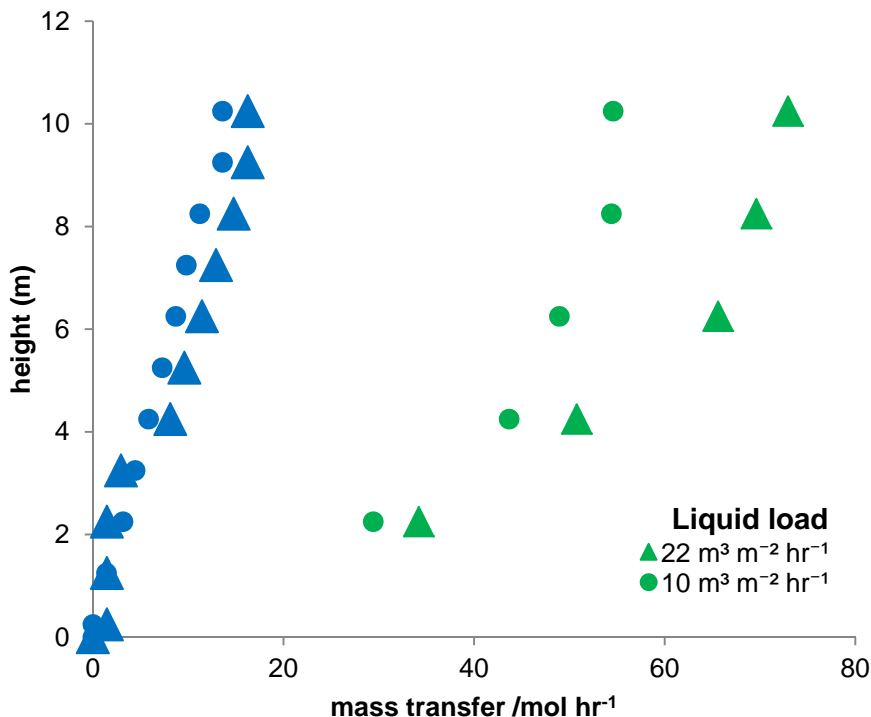


Figure 1: Mass transfer of  $\text{CO}_2$  in absorption experiments with 30 wt% MDEA as a function of column height; green symbols correspond to experiments with CA, blue to MDEA solution without enzyme.

The effect of CA addition on the absorption can be seen in Figure 1. The results from the MDEA campaign are calculated based on a mass balance over the liquid phase using the liquid samples from experiments over the full column height. The experiments for CA are actual measured mass transfer data. In this graph it can be seen that the addition of CA to the solvent increased the mass transfer significantly. The highest mass transfer was achieved at higher liquid loads ( $\text{m}^3 \text{m}^2 \text{hr}^{-1}$ ). Likewise, the increase in column height resulted in an increase in absorption, while at a liquid load of  $10 \text{ m}^3 \text{m}^2 \text{hr}^{-1}$  the difference diminishes between 8 and 10 m column height. An increase in liquid load resulted in higher mass transfer in all experiments. This can be explained by the fact that the mass transfer area in a packed column increases with liquid load [12], [13]. From Eq. (2) it can be seen, that a higher mass transfer area results in higher mass transfer.

The same amount of transferred  $\text{CO}_2$  will result in a lower  $\text{CO}_2$  concentration in the liquid phase, when more liquid solvent is in the absorber column. Thus when running the absorption at a higher liquid load the concentration of  $\text{CO}_2$  will be lower and therefore the driving force for the mass transfer (numerator in Eq. (2)) will be higher.

### 3.2. Liquid load and lean loading

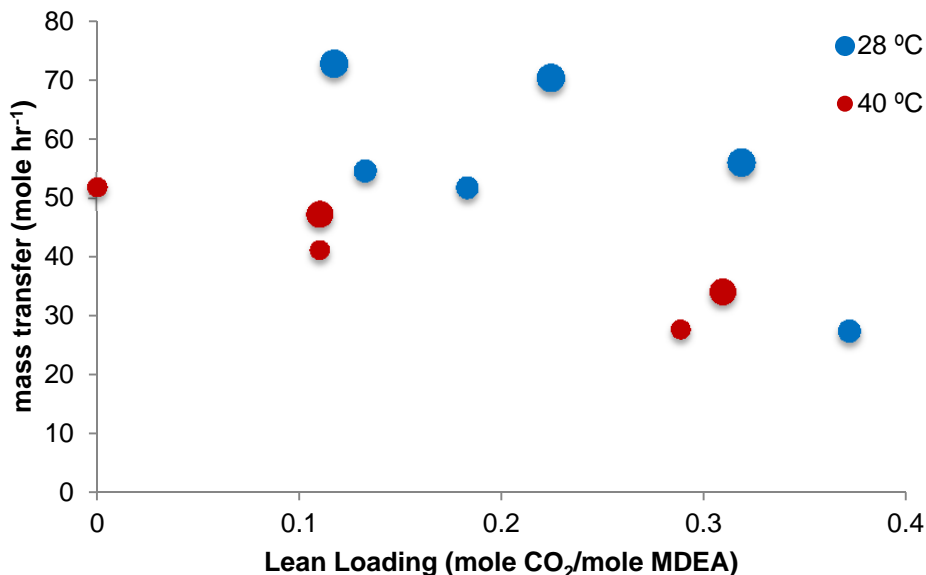


Figure 2: Effect of lean loading on absorption of  $\text{CO}_2$ , big symbols are corresponding to a liquid load of  $22 \text{ m}^3 \text{m}^2 \text{hr}^{-1}$ , small symbols to  $10 \text{ m}^3 \text{m}^2 \text{hr}^{-1}$

A higher absorption temperature resulted in a lower absorption as shown in Figure 3. Both for a liquid load of 10 and  $22 \text{ m}^3 \text{m}^2 \text{hr}^{-1}$  more  $\text{CO}_2$  could be absorbed when the absorption inlet temperature was 28 instead of 40 °C. The increase in liquid load also led to a higher mass transfer of  $\text{CO}_2$ . This effect was more distinct at low temperatures. The temperature effect might also be explained by the thermodynamics of the solvent. The mass transfer is proportional to the driving force, which can be described as the difference in partial pressure of  $\text{CO}_2$  in the gas phase and the liquid phase. The partial pressure of  $\text{CO}_2$  in the liquid is dependent on composition as well as temperature. When comparing two liquid solvents with the same composition at different temperatures, the solvent at the higher temperature will exhibit a higher partial pressure of  $\text{CO}_2$ . The driving force of a solvent at higher temperature will therefore diminish faster upon loading of the solvent. Another reason for higher absorption at lower temperature is

that the mass transfer of CA enhanced MDEA was found to have slightly higher mass transfer at lower temperatures [14].

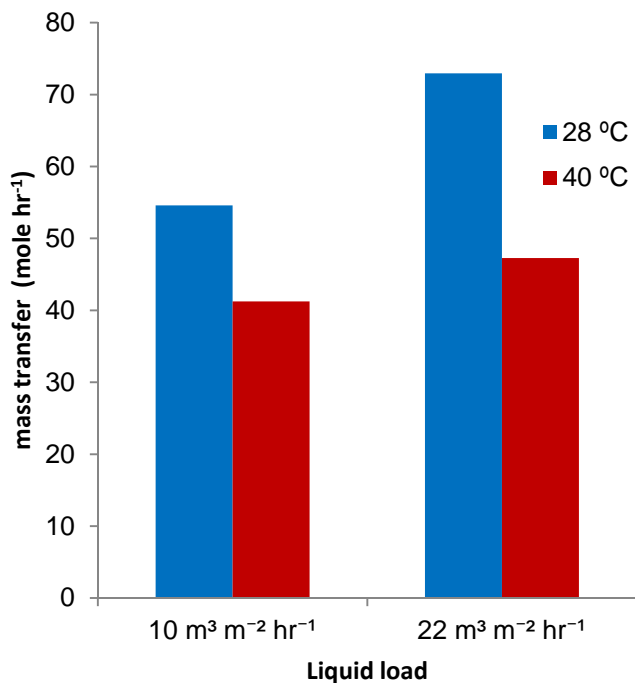


Figure 3: Effect of temperature on the mass transfer of  $\text{CO}_2$  into 30 wt% MDEA at a lean loading of about 0.1 mole  $\text{CO}_2$  per mole of MDEA

The same tendency of liquid load and temperature on mass transfer could be observed at different lean loading of the solvent as shown in Figure 2. Absorption at 28 °C always resulted in higher absorption at comparable loading. The mass transfer decreased when the lean loading increased for both temperatures.

### 3.3. Desorption experiments

After the solvent was loaded (up to the equilibrium concentration) for a gas partial pressure of about 13 kPa at 28 °C, the solvent was heated up and desorption experiments were carried out using air as a strip gas. Three experimental campaigns were conducted, one with plain 30 wt% MDEA, and two with CA enhanced MDEA solvent. The experiments with plain MDEA were performed at 55 °C, whereas the runs with CA enhanced MDEA were performed at 45 and 50 °C. All experiments were performed at different column heights between 2 and 10 m. In Figure 4 it can be seen that CA also catalyzes the desorption, as higher mass transfer was observed for the solvents containing CA. This effect might be even more distinct, as the temperature in the desorption with solvents containing CA was lower than for the experiment with plain MDEA. A clear increase in desorption for CA enhanced solvents was observed when the desorption temperature was increased from 45 to 50 °C. At smaller column heights (beneath 6 m) the mass transfer increased with each section, whereas for column heights larger than 6 m almost no effect of additional column height was observed.

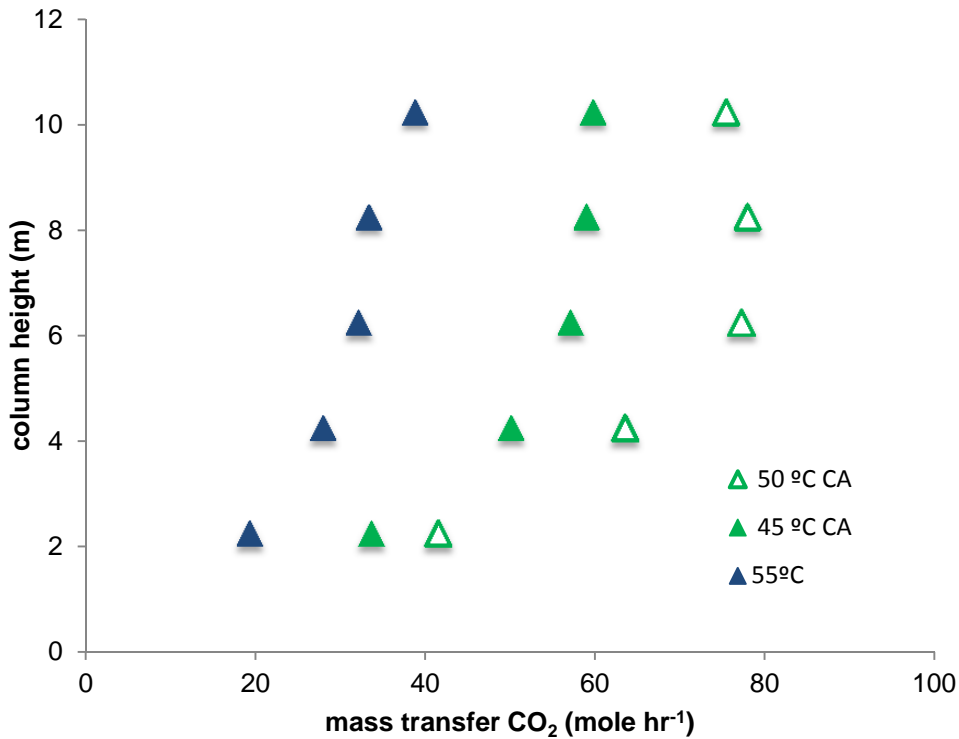


Figure 4: Mass transfer in stripgas desorption experiments, green symbols refer to experiments with CA

#### 4. Conclusions

The enzyme carbonic anhydrase is capable of being applied in mass transfer unit operations at pilot scale and can significantly increase absorption and desorption rates. The absorption rates could be increased by using a higher liquid load or a lower absorption temperature. The lean loading of the solvent resulted in a decrease in mass transfer during absorption. For optimal conditions the absorption should be carried out at low temperature, low lean loading and a high liquid load in the absorber. As expected, the experiments also showed that the enzyme carbonic anhydrase catalyzes the reverse reaction and enhances the desorption process.

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