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Pilot scale absorption experiments with carbonic anhydrase-enhanced MDEA- Benchmarking with 30 wt% MEA

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Highlights:

Keywords:

Pilot scale, carbonic anhydrase, carbon capture, MEA, MDEA

Abstract:

In this study the CO₂ mass transfer performance of enzyme enhanced MDEA solutions were benchmarked against the industrial standard 30 wt% MEA solution on a pilot packed column (10 m height, 0.1 m diameter). For all 64 experiments (18 for MEA and 46 for enzyme enhanced MDEA) relevant process data for process modelling such as flow rates, temperatures and inlet compositions as well as the overall mass transfer flux were measured. For 18 MEA experiments and 15 enzyme enhanced MDEA experiments temperature profiles of the column and solvent loading profiles were obtained. In experiments with MEA the column height and the liquid to gas mass flow ratio (L/G) were altered, whereas for enzyme enhanced MDEA in addition to column height and L/G ratio, the effect of enzyme concentration, solvent loading and temperature on the capture efficiency were determined. The experiments clearly show the positive effect of the enzyme addition on CO₂ capture efficiency for the MDEA solvent which can be further increased by adding more enzyme. Enzyme enhanced solvents exhibited around 80 % of the mass transfer performance of a 30 wt% MEA solvent solution.

1. Introduction

Enzyme enhanced CO₂ capture targets one of the main obstacles of carbon capture and storage technology (CCS): the high energy demand for solvent regeneration in the chemical absorption process. Currently only primary and secondary amines are considered as suitable solvents, as their direct reaction mechanism with CO₂ to form carbamates is fast enough to result in sufficient mass transfer rates. These solvents however require higher energy input in the desorption process to reverse the reactions [1] compared to tertiary amines. The slow base catalyzed reaction mechanism of the tertiary amines makes this solvent group unattractive for CCS from point sources with low CO₂ partial pressures such as fossil fuel fired power plants, as column heights of several hundred meters would be required for a 90 % CO₂ capture [2]. The enzyme carbonic anhydrase (CA) which catalyzes the hydration of carbon dioxide forming bicarbonate in aqueous solutions can help to overcome the kinetic limitation of tertiary amines. Several authors have reported successful mass transfer enhancement by CA addition for various slow absorbing bicarbonate forming solvents [3]–[5] in lab scale and pilot scale [6], [7]. In order to evaluate the potential of this technology further experiments at pilot scale are needed. These experiments should also be benchmarked against proven technologies.

The aim of this paper is to provide experimental pilot plant data on enzyme enhanced CO₂ capture with a MDEA (N-methyl-diethanolamine) solvent suitable for process modelling. The experimental data exemplifies how the process parameters: column height, liquid to gas ratio (L/G), solvent loading, solvent temperature and enzyme concentration influence the CO₂ capture efficiency of enzyme enhanced MDEA at pilot scale. A second set of experiments shows how the industrial standard for CCS, a 30 wt% MEA (monoethanolamine) solution performs under the same conditions on the same setup.

2. Experimental setup

The absorber column setup was previously used in the work of Sørensen et al. [8] with some modifications. The setup consists of three subsystems: the gas system, the liquid system and the column itself.

Figure 1: Scheme and dimensions of DTU's pilot absorber column setup; red lines indicate the gas system, and blue lines the liquid system.

The absorber column consists of 10 glass tubes with a height of around 1m each and an inner diameter of 0.1 m. They are connected with flanges, which incorporate a patented liquid sampling system [9] and are equipped with a temperature sensor. At every second flange there is a liquid inlet, while every other flange has a liquid recollector built in, which transfers the liquid away from the wall towards the center of the column. The height of each glass tube including the flange is approximately 1 m; thus the whole glass section is about 10 m high. The liquid inlets are at heights of 2, 4, 6, 8 and 10 m height, the liquid recollectors at heights of 1,3,5,7 and 9 m. Each 1 m glass section is filled with 4 structured packing elements of the type Mellapak 250 Y each

with a diameter of 0.084 m and a height of 0.205 m. The packing elements are fixed with liquid recollectors inside the glass column, that prevent the gas from bypassing the packing at the wall and which recollect the liquid phase from the wall. The total packed height is 8.2 m and the packing volume is 0.0454 m³. The distance between the gas and liquid inlet is 10.25 m thus the total column volume is 0.0805 m³.

The differential pressure to the outside atmosphere is measured at the base of the column, the middle (5m) and the column head. The gas is introduced into the column 0.25 m below the packing with an open-ended pipe. The liquid is distributed into the column with a round spray nozzle with 18 drip points, corresponding to about 1400 drip points per square meter. The drip points are positioned so that they distribute the liquid uniformly over the cross section. The column has no sump; the liquid is pumped directly into a storage tank. The glass sections are insulated with 13 mm Thermaflex to limit heat losses during experiments.

The gas system covers the handling of the gas outside the column. In these experiments the gas phase was a closed loop driven by a fan. Only CO₂ was added to the system by gas bottles. The recycle ensures that the gas stream is saturated at the inlet conditions and minimizes CO₂ and N₂ usage. The gas flow was regulated by the fan speed. At the column inlet and outlet, CO₂ concentration (Vaisala Carbocap), absolute pressure and temperature of the gas phase were measured. A Coriolis flowmeter measured the total mass flow of gas entering the column and another Coriolis flowmeter situated at the gas bottle tracked the amount of CO₂ being added to the system.

The liquid was mixed in a 400 L mobile tank equipped with a heating jacket and pumped around with a centrifugal pump. The temperature as well as the mass flow was measured with a PT probe and a Coriolis flowmeter before the liquid inlet.

In order to characterize the experimental setup several experiments have been conducted to determine crucial mass transfer parameters.

2.1. Holdup determination

Liquid hold up describes the amount of liquid inside the absorber; the value is dependent on the liquid flow, gas flow and the column packing. The experiments were carried out with air and water. A certain liquid and gas flow was initially set. At the exact same time the liquid and gas inlet was stopped and the liquid exiting the column was collected for 5 minutes after the turn down. In order to eliminate end effects at the liquid outlet two runs were performed at the same gas and liquid setpoints, one with 10 m column and one with 2 m column height. The amount of water collected at 2 m column height was subtracted from the amount of water collected at 10 m column under the same conditions. The holdup (difference) was then correlated to the 8 m packing between the two measurement points. All experiments were carried out in triplicate.

Figure 2: Liquid hold up as a function of gas capacity factor for different liquid loads

The column holdup as a function of the gas capacity factor for different liquid loads is shown in Figure 2. The liquid holdup is increasing with liquid load. The gas capacity factor ($F_v = u_G \sqrt{\rho_G}$) does not influence the hold up for low values. At a certain gas capacity the holdup increases and the column starts loading. This loading regime occurs at lower gas capacities when the liquid load is increased, as the experiments with $64 \text{ m}^3 \text{ m}^{-2} \text{ hr}^{-1}$ are already in the loading regime at a gas capacity of around $1 \text{ Pa}^{0.5}$, whereas all other experiments were still outside the loading regime. The holdup of the column as a function of the hydrodynamics (liquid load, gas capacity) follows the same trend as examples from literature [10], [11].

Suess and Spiegel determined experimentally the holdup for different Mellapak structured packings [12]. They could derive an empirical correlation for the holdup below the loading point. The comparison of their literature correlation with our experiments is shown in Figure 5. The literature correlation is about 10 % lower than the experiments. This difference might occur from the liquid volume that accumulated in the free spaces between the packing, as there was just 0.82 m packing height per meter of column.

Figure 3: Liquid holdup in the column below the loading regime.

2.2. Mass transfer area determination

The mass transfer area is very crucial for the dimensioning of mass transfer unit operations and sometimes differs widely from the geometric surface of the packing [10]. It is not possible to simply measure the mass transfer area inside the absorber during operation. Only the mass transfer inside a column can be measured by making a material balance over the column. Where the mass transfer resistances and driving forces are known the effective mass transfer area can be calculated from the total mass transfer flux of CO₂. A standard procedure for mass transfer area determination in absorber columns is the absorption of highly diluted CO₂ (≈ 1 vol% CO₂) into concentrated NaOH (≈ 1 M NaOH) at high gas velocities [13], [14]. The low CO₂ concentration in the gas phase and the high concentration of NaOH in the liquid phase ensure that the chemical absorption follows a pseudo first order behavior. Thus the OH⁻ concentration is the same at the interface as in the liquid bulk. The high gas velocity reduces the influence of gas side mass transfer resistance on the overall mass transfer resistance. The gas side mass transfer resistance might be neglected at gas velocities above 0.5 m s⁻¹ in experiments for interfacial mass transfer area determination [14].

Kunze et al. [13] derived a standardized procedure for the determination of mass transfer parameter for absorption. The effective area a_{eff} (m² m⁻³) can be calculated according to them as:

$$a_{eff} = \frac{\frac{V_G}{H \cdot a_{CS}} \ln \frac{y_{CO_2}^{in}}{y_{CO_2}^{out}}}{\sqrt{\frac{D_{CO_2} \cdot C_{OH^-} \cdot k_{OH^-}}{m_{CO_2}}}} \quad (1)$$

This expression uses a dimensionless Henry's coefficient m_{CO_2} that can be calculated from H_{CO_2} ($\text{Pa m}^3 \text{ mol}^{-1}$) applying the ideal gas law:

$$m_{CO_2} = \frac{C_{CO_2}^G}{C_{CO_2}^L} = \frac{\frac{n_{CO_2}^G}{V}}{C_{CO_2}^L} = \frac{\frac{P_{CO_2}}{R \cdot T}}{C_{CO_2}^L} = \frac{H_{CO_2}}{R \cdot T} \quad (2)$$

Figure 4: Mass transfer area measured in CO_2 absorption experiments with 1 M NaOH at 2-6 m column height; dotted line indicates the surface area of Mellapak 250 Y inside the column

The results from the mass transfer area determination experiments with 1 M NaOH at 2, 4 and 6 m column height with gas velocities ranging from 0.5 to 0.9 m s^{-1} are shown in Figure 4. The theoretical mass transfer area was calculated as the ratio of packing surface and total volume of the column and has the value of $141.12 \text{ m}^2 \text{ m}^{-3}$. For high liquid loads at 2 m column an interfacial area higher than the theoretical value was measured. This might be explained by liquid running down inside the outer wall of the column. The surface area of the wall on the outer shell is generally not considered in calculations for the interfacial area, as for large columns its contribution is marginal. For lab and pilot scale columns with small diameter the contribution of the inner surface of the column to the total interfacial area might be significant. Considering that the whole inside of the glass tube is also mass transfer surface, by adding $\text{diameter} \cdot \pi \cdot \text{height}$ to the mass transfer area of the column will increase the theoretical mass transfer area to $181.12 \text{ m}^2 \text{ m}^{-3}$ a value almost 30% higher than the surface of the structured packing. Smaller specific mass transfer areas have been observed at higher column heights. This decline might arise from maldistribution with liquid accumulating at the column walls [15]. As the column has no liquid redistributors over the height which spreads out the liquid phase homogenously, the maldistribution might be more profound at higher column heights. Another reason for the decrease of specific mass transfer area might be that some of the assumptions do not hold for higher column heights. The calculation method assumes pseudo first order reaction regime

between the hydroxide ion and CO₂, which states that the concentration of hydroxide ions at the mass transfer interface and liquid bulk are the same. It also assumes that the hydroxide ion concentration at the liquid inlet and the liquid outlet are the same. In case the hydroxide ion concentration is changing either inside the mass transfer film or over the height of the column the formula in Eq. (1) is not correct. Further experiments are needed to address whether maldistribution or change in hydroxide ion concentration causes the change in mass transfer area measured at different column heights.

3. Material and Methods

3.1. Chemicals

The solvent MEA was obtained from Brenntag A/S and MDEA from BASF. Both solvents were mixed with DI water to result in a 30 wt% aqueous amine solution. For the MEA solvent preparation part of the solvent was loaded with CO₂ and then mixed with unloaded solvent solution in order to result in a solvent loading of 0.24 and 0.29 mol CO₂ per mol amine. For the enzyme solvent solution part of the water was exchanged with liquid carbonic anhydrase enzyme solution on mass basis. The MDEA solvent solution was slightly loaded with CO₂ prior to enzyme addition to avoid very high pH values of unloaded amine solutions. The amine content of the amine solvent solutions was checked with an acid titration using 0.5 N HCl. The solvent loading at the inlet and the outlet of the column during experiments was determined with and BaCl precipitation method. For the solvent loading profiles over the height of the column a density model was used as explained in the next section.

3.2. Density model for solvent loading determination

The amount of liquid samples derived from pilot plant experiments was very high, a solvent loading determination method such as the BaCl titration method of Snderby et al. [8] would be too time-consuming. The solvent loading in the column profiles was therefore correlated by the solution density. This method has worked very accurately for MEA solutions on our pilot plant [16] using the density model from Weiland et al. [17].

The Weiland model correlated the density as ratio of average molecular weight and total volume. In order to work for enzyme containing solutions, their expression was extended by a CA term for the molecular weight and the volume, leading to the following form:

$$\rho = \frac{x_{Am} \cdot M_{Am} + x_{H_2O} \cdot M_{H_2O} + x_{CO_2} \cdot M_{CO_2} + x_{CA} \cdot M_{wCA}}{x_{Am} \cdot V_{Am} + x_{H_2O} \cdot V_{H_2O} + x_{CO_2} \cdot V_{CO_2} + x_{CA} \cdot V_{CA} + x_{Am} \cdot x_{H_2O} \cdot V^* + x_{Am} \cdot x_{CO_2} \cdot V^{**}} \quad (3)$$

With x_i being the molefraction, and V_i the molar volume of the different solvent compounds. The non-ideality of the density is accounted for with an interaction parameter for water amine interaction V^* and for CO₂ amine interaction V^{**} . The molar volume and amine-CO₂ interaction parameter can be calculated from constants given in their paper. It was assumed that CA

interaction did not create another excess molar volume. The molecular volume for CA was calculated from the results of a X-ray diffraction data for hCA-II [18]:

$$V_{CA} = \frac{A \cdot a \cdot b \cdot c \cdot \sin \beta}{z} = 0,0722 \frac{m^3}{mole} \quad (4)$$

Where A, is the Avogadro's constant, a, b and c are the cell axis dimensions of a unit cell, β is the inclination of the a-axes in the unit cell and z is the number of molecules in a unit cell all values are listed in the work of Robbins et al. [18]. It was assumed that the molar volume of CA does not change with temperature. An average molecular weight of 30 000 g mol⁻¹ was assumed for CA.

The results of the extended Weiland model in comparison to experimental data at 298 K are shown in Figure 5. The solution densities were measured with a DMA 230 Anton Paar with an accuracy of ± 0.0001 g cm⁻³.

A clear increase in solvent density can be observed with higher solvent loading. The density of the blue circles indicating 30 wt% MDEA without enzyme can predicted very accurately with the Weiland model (blue line). The density of the solution slightly decreased when 1.8 g/L CA were added (red circles); this effect could be captured by the extension of the Weiland model (red line). This extended model was also capable to describe the density of a 15 wt% and 50 wt% MDEA solutions as function of solvent loading with 1.8 g/L CA added.

Figure 5: Density of solution as a function of solvent loading, for 15, 30 and 50 wt% MDEA with 1.8 g/L CA at 298 K. Comparison between experimental results and extended Weiland et al. model [17]

The extended Weiland model was validated against density data from 15, 30 and 50 wt% MDEA at 298, 313 and 328 K with 0.85 and 1.8 g/L CA concentration at different solvent loadings. The results are shown in Figure 6. The extended model was capable to describe the solutions density

very accurately for process temperatures between 298-328 K and 15-50 wt% MDEA with up to 1.8 g/L CA concentration.

Figure 6: Parity plot of the extended Weiland model at 298 to 328 K and 0.9 and 1.8 g/L CA; blue symbols correspond to 15 wt% MDEA, red symbols to 30 wt% MDEA and green symbols 50 wt% MDEA, dashed lines indicated ± 2 % deviation.

3.3. Material balance

The amount of CO₂ transfer was calculated from the reading and measurements on the column for the gas and the liquid phase. For the gas phase the following formula was applied:

$$\Delta N_{CO_2}^G = y_{CO_2}^{in} N_{Gas}^{in} - y_{CO_2}^{out} N_{Gas}^{out} \quad (5)$$

The mole fractions of CO₂ were measured with the NDIR probes and corrected for pressure and temperature [19]. The molar flux of CO₂ going into the column can be calculated from the mass flow of the coriolis flowmeter knowing the composition comprising water vapor, carbon dioxide and nitrogen. The molar fraction of water was calculated from the water vapor pressure. It was assumed that the gas stream is saturated with water vapor as the gas was recycled in a closed loop. Only the molar flow of nitrogen was assumed to be constant inside the column, as CO₂ was absorbed and water might be evaporated inside the column. The total molar gas flow was calculated from the material balance of nitrogen over the column:

$$\Delta N_{N_2}^G = 0 = y_{N_2}^{in} N_{Gas}^{in} - y_{N_2}^{out} N_{Gas}^{out} \quad (6)$$

This leads to the following expression for total gas flow exiting the column:

$$N_{Gas}^{out} = \frac{y_{N_2}^{in} N_{Gas}^{in}}{y_{N_2}^{out}} \quad (7)$$

The mole fraction of nitrogen was calculated from the mole-fractions of the other two compounds, as they add up to 1.

The material balance over the liquid phase was calculated from the molar flow of solvent and the solvent loading:

$$\Delta N_{CO_2}^L = \alpha_{CO_2}^{in} N_{sol}^{in} - \alpha_{CO_2}^{out} N_{sol}^{out} \quad (8)$$

It was assumed that the amount of solvent evaporating inside the column was negligible, thus the incoming and outgoing molar flow of solvent is the same and can be calculated from the mass fraction of solvent, the molecular weight and the mass flow reading from the Coriolis flow meter.

3.4. Experimental procedure

The column was flushed with pure N₂ from a bottle before the experiments in an open loop. A small amount of CO₂ was added at the start to check the residence time of the gas inside the column. The flushing procedure was continued for 15 minutes after the last traceable CO₂ was measured in gas outlet of the column. The gas was loop was then closed and the fan was started. CO₂ was added until 12-14 vol.% could be detected at the in- and outlet, with both CO₂ measuring the same value. The right gas flow for the experiments was set in the fan and the liquid pump was started. Once the liquid was introduced into the column at the right position the CO₂ feed from the bottle was adjusted. After 10 minutes steady state for the inlet and outlet CO₂ concentrations as well as the gas and liquid mass flow rates was obtained, samples for the inlet and outlet loadings and occasionally also liquid samples over the height of the column were taken. The setpoints for the experiments were changed after taking the samples and a new steady was achieved. The time to reach a steady state in the experiments was between 10-30 min.

3.5. Experimental campaigns

Three different experimental campaigns have been carried out, one with 30 wt% MEA, one with 30 wt% MDEA with 0.85 g/L CA and one with 30 wt% MDEA and 3.5 g/L CA. The gas load, described as volume flow of gas per cross-section of column (0.1 m diameter), was kept constant in each campaign with high gas velocities of more than 0.5 m s⁻¹, in order to limit the influence of the gas side mass transfer resistance on the overall mass transfer. The CO₂ inlet volume concentration was adjusted to a value between 12-14 vol%. The L/G ratio was changed by altering the liquid load in the experiments. All L/G ratios reported here are mass flow ratios of total liquid mass flow to total gas mass flow in kg/kg unless otherwise stated. The capture efficiency was calculated from the gas in- and outlet concentrations and describes the amount of CO₂ being captured inside the column.

For the MEA solvent the effect of column height as well as L/G ratio on the CO₂ capture efficiency was determined. The solvent solution was not preheated and had an inlet temperature around 25 ° C. The inlet loading for experiments at 2 and 4 m column height was 0.24 mol CO₂ per mole MEA. The inlet solvent loading was increased for MEA experiments at 6, 8 and 10 m column height to 0.29 mol CO₂ per mol of MEA to result in capture efficiencies below 100 % in

the experiments. The L/G was altered by just changing the liquid flow rate. The gas load was kept constant at around $0.8 \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$. The L/G ratio in the MEA experiments was between 1.8 and 6.3, which correspond to liquid loads between 5.9 and $20.9 \text{ m}^3 \text{ m}^{-3} \text{ hr}^{-1}$. Temperature as well as solvent loading profiles was derived from the experiments and the capture efficiency was calculated.

In the experimental campaign with 30 wt% MDEA and 0.85 g/L CA the capture efficiency at different column heights (2-10 m) was determined for 3.3 and 7.7 L/G ratio (kg/kg) at 28 and 40 °C. At 10 m column height additional experiments at different lean loadings were performed to determine the effect of solvent loading on the capture efficiency. The gas load was kept constant at around $0.7 \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ while the liquid was varied between 8.5 and $21.3 \text{ m}^3 \text{ m}^{-3} \text{ hr}^{-1}$. Some runs were performed at room temperature ranging from 25 to 28 °C, for other runs the solvent solution was preheated to 40 °C. In this campaign the liquid phase was recycled to the absorber, thus the loading changed throughout the experiments. The total amount of solvent was 350 kg and the maximum flow was 175 kg/hr. Therefore within the 10 min steady less than 10% of the solvent inventory was exchanged and it was not assumed that changes in composition had affected the experiments.

For the campaign with 30 wt% MDEA and 3.5 g/L CA the effect of column height (2-10 m) on the CO₂ capture efficiency for 4.5 L/G ratio (kg/kg) was determined for a lean loading of 0.07 and 0.27 mole CO₂ per mole of MDEA molecule. The gas load was kept constant at $0.8 \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ and the liquid load was varied between 8.5 and $30.3 \text{ m}^3 \text{ m}^{-3} \text{ hr}^{-1}$ leading to L/G ratios between 2.6 and 9.3. At 10 m column height also full solvent loading and temperature profiles were taken. The solvent solution was used at room temperature which was around 26 °C. the experiments with 3.5 g/L CA were performed without solvent solution recycle.

The exact values for gas and liquid flow rates as well as compositions of the flows and temperatures can be found in the Appendix: under A for 30 wt% MEA, under B for 30 wt% MEA with 0.85 g/L CA and under C for 30 wt% MDEA with 3.5 g/L CA. The CO₂ capture efficiencies of the experiments are collected under D in the Appendix.

4. Results and discussion

4.1.MEA campaign

The L/G ratio had a significant influence on the temperature as well as solvent loading profiles over the height of the column, as shown in Figure 7 for experiments with 6-8 m column and in Figure 8 for experiments with 10 m column height. In all experiments with 30 wt% MEA a temperature bulge could be observed in the column. The temperature bulge was located in the top of the column for experiments with low L/G ratios (i.e. low liquid loads) and wandered down when the L/G ratio was increased by increasing the liquid load. This phenome could be observed for all experiments with column heights between 6 and 10 m. The solvent loading profiles inside the column revealed that some areas of the column were more active in mass transfer than others. For low L/G ratios (2.4-2.7) the increase in solvent loading over the height of the column was

higher in the top part of the column as the profile is shallower in that region which implies that more mass transfer of CO₂ occurred there. When the L/G ratio was increased to a medium value (4.3-4.4) for experiments at 6-8 m column height a close to linear solvent loading profile could be observed which represents a homogenous mass transfer over the height of the column. At a high L/G ratio (6.1-6.2) the solvent loading profile was steeper in the top of the column and shallower in the bottom part demonstrating a higher mass transfer of CO₂ in the bottom part of the column. The most active part in mass transfer in the absorber column migrated down from top to bottom when the L/G ratio was increased from a low to a high value, similar to the temperature peak observed inside the column.

The temperature profiles inside the column are influenced by several effects. The exothermic reaction between MEA and CO₂ increases the temperature of the liquid phase. The enthalpy is transported downwards in the liquid phase by gravitational forces. When the gas phase has a lower temperature than the liquid phase water and small amounts of solvent evaporate. This effects cools down the liquid phase and heats up the gas phase. The gas phase transports an enthalpy stream upwards. The warm saturated gas streams then condensate onto cool liquid streams in the upper part of the column. These interactions result in formation of temperature bulges [20]. Several other authors have observed temperature bulges in pilot absorption experiments with 30 wt% MEA [20]–[23]. The highest temperatures inside the column could be observed at the lowest and the medium L/G ratio (2.4-2.7 and 4.3-4.4). At 8 m column height the total temperature increase was higher than at 6 m column height, because in total more CO₂ was absorbed at higher heights which could be also observed in a higher rich solvent loading at the liquid outlet.

Figure 7: Temperature (left) and solvent loading (right) profiles for pilot experiments with 30 wt% MEA, 0.29 (mol/mol) inlet loading and 25 °C inlet temperature for 6 and 8 m column height at different L/G ratios

A similar correlation between L/G ratio and position of the temperature bulge could be observed in absorption experiments at 10 m column height. The size of the temperature bulge increased

when the L/G ratio was increased from a low to a medium value. A further increase in L/G ratio led to smaller temperature bulge. A maximum temperature of 68 °C was measured at an L/G ratio of 4.5, which represented an increase of 43 °C temperature compared to the inlet temperature. In all experiments the areas with the highest mass transfer were near the temperature bulge. If the temperature bulge was in the middle of the column the mass transfer was equally distributed over the column. Experiments at low L/G ratio have a rich end pinch, as there is not sufficient solvent available to capture all of the CO₂ the solvent is loaded to equilibrium. This can explain why the total temperature inside the column was lower at low L/G ratios than at medium L/G ratios.

Figure 8: Temperature (left) and solvent loading (right) profiles for pilot experiments with 30 wt% MEA, 0.29 (mol/mol) inlet loading and 25 °C inlet temperature for 10 column height for different L/G ratios

The capture efficiencies of the MEA campaign as a function of the L/G ratio for the different column heights are shown in Figure 9. An increase in L/G ratio always resulted in a higher CO₂ capture efficiencies. An increase in column height likewise led to a higher CO₂ capture efficiency. The effect of column height seems to be diminishing at higher heights, as the increase of CO₂ capture efficiency by an additional 2 m is very high between 2 and 4m and quite low between 8 and 10 m.

At low L/G ratios higher CO₂ capture efficiency could be obtained at 4 m than at 6m. This effect can be explained by the different solvent solutions used in the two experiments. While the solvent loading was 0.24 mol CO₂ per mol MEA in the experiments at 4 m, it had a lean loading of 0.29 for experiments at 6-10 m. At a higher L/G a higher CO₂ capture efficiency could be achieved for all experiments performed on the same column height.

When the two solvent solutions at different loadings are compared a higher influence of L/G on the capture efficiency can be observed for the higher loaded solvent as the trends are steeper. A CO₂ capture efficiency higher than 90 % could be achieved at 8 and 10 m column height for high L/G ratios. The minimum L/G ratio to reach more than 90 % CO₂ capture was 5.4 for 10 m

column height and 6.3 for 8 m column height; at 10 m column height with 4.5 L/G ratio the CO₂ capture efficiency was just 1 % below the 90 % CO₂ capture threshold.

Figure 9: Capture efficiency as function of L/G ratio for absorption experiments with 30 wt% MEA at 25 °C inlet temperature and 0.24 lean loading at 2-4 m (left) and 0.29 lean loading at 6-10 m (right).

4.2. MDEA campaigns

Experiments with enzyme enhanced MDEA at different column heights have been conducted where the effect of L/G ratio as well as solvent lean loading on CO₂ capture efficiency has been looked at. The result of the CO₂ capture efficiencies for experimental runs with 30 wt% MDEA with 0.85 g/L CA at different column heights for 3.3 and 7.3 L/G ratio are shown on the left side of Figure 10. A higher L/G ratio led to a higher CO₂ capture efficiency; at higher column heights this effect. An increase in column height likewise increased the CO₂ capture efficiency. At higher column heights and low L/G ratios an increase in column height will most likely not increase the performance as the CO₂ capture efficiency could be increased just by 1% point from 39 to 40 %, when the height was increased from 8 to 10 m. For 7.7 L/G the increase was 3 % points from 53 % to 56 % when the column height was increased in the same range.

When the solvent loading is increasing the equilibrium partial of the liquid phase is rising. When the gas and the liquid have the same CO₂ equilibrium partial pressures no mass transfer occurs. This mass transfer pinch might happen in the top of the column, called lean end pinch, where the gas exiting the column is in equilibrium with the solvent being fed into the top of the column. When the liquid solvent solution going out of the column is in equilibrium with the gas stream entering the column the column has a rich end pinch. When pinch conditions occur in absorption the mass transfer cannot be increased by a higher column height. For the experiments with 30 wt% MDEA and 0.85 g/L CA at an L/G ratio of 3.3 the small increase in CO₂ capture efficiency between 8 and 10 m column height can be explained with the system approaching a rich end

pinch, as the rich solvent loading was 0.39 mol CO₂/ mol MDEA at 8 m height and 0.4 mol CO₂/ mol MDEA at 10 m height which is close to the thermodynamic equilibrium of the solvent solution which is around 0.43 at 40 °C [24]. In that case the solvent cannot take up more CO₂ anymore.

For the experimental campaign with 30 wt% MDEA and 3.5 g/L CA the effect of solvent lean loading on the CO₂ capture efficiency has been investigated, the results are shown in Figure 10 on the right side. A higher lean loading decreased the CO₂ capture efficiency from 65 to 43 % at 10 m column height. For the higher loaded solvent a limiting trend could be observed for higher column heights, as the CO₂ capture efficiency for 8 m was almost the same as for 10 m (43 % and 42 %). A reason for that behavior might be that the system is close to a rich end pinch with 0.37 mol CO₂/ mol MDEA solvent loading. Another effect at a higher inlet loading that might influence the mass transfer is that the system is also approaching the lean end pinch. For the lower loaded solvent it seemed that an increase in column height would potentially increase the capture efficiency further. The results shown in Figure 10 visualize how the process conditions, column height, L/G ratio as well as solvent loading are affecting the CO₂ capture efficiency in enzyme enhanced CO₂ capture. The exact values are listed in Table 18 and Table 19.

Figure 10: Capture efficiencies for 30 wt% MDEA solution with 0.85 and 3.5 g/L and 26 °C inlet temperature as function of column height for different L/G ratios (left) and different lean loadings (right)

Comparing the experiments on the left side and right side which were carried out at different enzyme concentrations showed, that at a higher L/G ratio (7.7 vs. 4.5) enzyme solvent with 0.85 g/L CA might be almost as effective as 30 wt% MDEA with 3.5 g/L CA, even though it also had a higher lean loading (0.13 vs 0.07). The influence of solvent lean loading on the capture efficiency at full column height (10 m) with 30 wt% MDEA and 0.85 g/L CA has been investigated further and the results are shown in Figure 11. On the left side the results from experiments with 28 °C inlet temperature and on the right side experiments with 40 °C inlet temperature are displayed. These results confirmed the trends were observed in the other

experiments as an increase in L/G ratio led to an increase and that an increase in solvent lean loading led to a decrease of the CO₂ capture efficiency. At similar lean loadings and L/G the capture efficiency for experiments at 28 °C was higher than for experiments at 40 °C. A similar tendency was observed by Leimbrink et al. [7] who reported higher mass transfer into enzyme enhanced 30 wt% MDEA at 20 °C compared to 40 °C. The reasons for that unusual absorption are on the one hand the absorption kinetics of enzyme enhanced MDEA and the solvent solutions thermodynamic. In our previous study we determined the absorption of CO₂ into various solvents and determined the effect of critical process conditions such as solvent concentration and solvent temperature on the mass transfer [19]. For enzyme enhanced MDEA we observed higher mass transfer rates into the solvent solutions at lower temperatures in the range of 25 to 55 °C. Even though the gas partial pressure might be the same for the experiments at 28 °C and 40 °C, the solvent solution at 40 °C has a higher equilibrium partial pressure when both solvents have the same loading. This will lead to different driving forces in the experiments at different temperatures which favors the low temperature process.

Figure 11: Influence of solvent lean loading on capture efficiency of 30 wt% MDEA solutions with 0.85 g/L CA for different L/G ratios at 28 °C (left) and 40 °C (right).

Full solvent loading and temperature profiles have been taken for experiments with 30 wt% MDEA with 3.5 g/L CA, 0.07 inlet loading and 26 °C inlet temperature. The results are shown in Figure 12, where the column temperature is displayed on the left side and the solvent loading on the right side. In temperature profile with the enzyme enhanced solvent also a temperature bulge could be observed. The position of the bulge although hardly changed with the L/G ratio and was located in the bottom of the column. The highest temperature increase of 16 °C was observed at the lowest L/G ratio, where a column temperature of 40 °C could be measured. The temperature values were much lower than the ones measured in the MEA campaign. The solvent loading profiles were also not much influenced by the L/G ratio as they were almost straight lines over the height of the column. Only the top part of the column (8-10 m) seemed a little less active than the rest of the column. This did not seem to be something specific caused by the enzyme, a

general lower performance in the highest two stages of the column might be a reason, as in the loading profiles with MEA in Figure 8 at low L/G ratios (1.8 and 2.8) also similar bend was visible.

Figure 12: Temperature and loading profiles for pilot experiments with 30 wt% MDEA, with 3.5 g/L CA and 0.07 (mol/mol) inlet loading and 26 °C inlet for different L/G ratios

5. Comparison of enzyme enhanced MDEA with MEA solvents solutions

It is difficult to compare different solvent technologies with each other when the performance experiments have been conducted on different setups. The goal of this study was perform pilot scale absorption experiments with enzyme enhanced MDEA as well as with the industrial standard 30 wt% MEA on the same equipment and benchmark their performances.

The results of the CO₂ capture efficiencies of the different solvents tested at 10 m column height as a function of L/G ratio are shown in Figure 13. It can be seen that 30 wt% MDEA without CA is a poor absorbing solvent for CCS applications, as the CO₂ capture efficiency ranged between 18 and 23 %. The addition of 0.85 g/L CA increased the mass transfer performance significantly; between 36 and 49 % of the CO₂ could be captured in the experiments. When the enzyme concentration was increased to 3.5 g/L the CO₂ capture efficiency increased even further. CO₂ capture efficiencies between 48 and 83 % were observed in these runs. Nonetheless the enzyme enhanced solvents did not reach or surpass the CO₂ capture efficiency of 30 wt% MEA. In the experimental runs with the industrial standard between 46 and 98 % of the CO₂ was captured inside the column. These experiments although show very clearly the positive effect of CA addition on the mass transfer. By the addition of 0.85 g/L CA the CO₂ capture efficiency of 30 wt% MDEA could be doubled. At 3.5 g/L CA concentration close three to four times the CO₂ capture efficiency of the blank MDEA solvent could be achieved. The experiments suggested that an increase in enzyme concentration would further increase the CO₂ capture efficiency and possible result in a higher mass transfer than 30 wt% MEA.

Only two literature sources reported capture efficiencies of 80 % or higher in pilot absorption experiments with enzyme enhanced solvents. Akermin Inc. performed field test run at the National Carbon Capture Center (NCCC) in Wilsonville Alabama. They were able to achieve 80% CO₂ capture with 20 wt% K₂CO₃ solvent at an L/G ratio of 7.88 (kg/kg) over a timeframe of 5 months [25]. The company CO₂ Solutions was also able to maintain a CO₂ capture efficiency of 80 % over 2500 hours with 20 wt% K₂CO₃ at 10.8 L/G ratio (kg/kg) [26]. Alvizio et al. performed absorption experiments at NCCC with 25 wt% MDEA solvent. In their 60 hour test run they were able to capture 60 % of the CO₂ from a flue gas stream containing 12 vol% CO₂ [27].

Kunze et al. [6] reported a catalytic effect CE, which describes how much faster the solvent became upon enzyme addition compared to the blank solvent without enzyme for 30 wt% MDEA and 2 g/L CA with values between 3.3 and 4.2 depending on the L/G ratio. They used the same enzyme from Novozymes in their experiments and reported similar increase of mass transfer performance at lower enzyme concentrations (2 g/L vs. 3.5 g/L). The CE value reported is useful to compare small scale experiments, where the process conditions (CO₂ partial pressure, solvent loading and temperature) do not change. In larger equipment like pilot columns all of these process conditions change over the height of the column. Especially with fast absorbing solvents these changes might be quite significant and limiting trends such as lean end or rich end pinch conditions might be approached which influence the mass transfer. In this study the mass transfer performance was benchmarked to 30 wt% MEA rather than 30 wt% MDEA. The results of the CO₂ capture performance of the different solvents tested compared to 30 wt% MEA are shown in Figure 14. The value was calculated by dividing the CO₂ capture efficiency of the MDEA solvent by the CO₂ capture efficiency of MEA solvent at a similar L/G ratio.

Figure 13: Capture efficiency as function of L/G ratio at 10.25 m column height for 30 wt% MEA and 30 wt% MDEA with 0, 0.85 and 3.5 g/L CA.

At larger column heights (6-10 m) the enzyme solvent with 0.85 g/L CA had about 55-57 % of the mass transfer performance of 30 wt% MEA. A 30 wt% MDEA solvent solution 3.5 g/L CA provided between 66 and 73 % of the mass transfer performance compared to 30 wt% MEA. Increasing the column height had just a very small positive effect on the absorption performance of the enzyme enhanced compared to MEA. The mass transfer performance of the solvents at smaller column heights (2-4 m) was lower. The difference can be explained by the different MEA solvent loading used in these experiments and therefore the benchmark was different in these experiments. At 10 m column height the influence of the L/G on the absorption performance has been investigated. While blank 30 wt% MDEA solvent was just capable to capture between 18 and 23 % of the CO₂ at 10 m column height in the absorption experiments, the same solvent with 0.85 g/L CA added reached CO₂ capture efficiencies between 36 and 49 % in a similar L/G ratio range. The trend of the experimental points for this solvent indicates a minimum at a medium L/G ratio, as better performances could be obtained at a lower and a higher L/G ratio. This behavior results most likely from the fact that the experiments with MDEA and MEA have not been carried out at the exact same L/G ratios. When the CA concentration was increased to 3.5 g/L even capture efficiencies between 48 and 78% could be observed. The trend suggests that this performance could be further increased by increasing the L/G ratio and the even 80 % could be surpassed for very high L/G ratios. In that region the MEA solvent would have 100 % capture efficiency and could

Figure 14: Mass transfer performance of 30 wt% MDEA and enzyme enhanced 30 wt% MDEA compared to the industrial standard 30 wt% MEA as a function of column height (left) and L/G ratio at full column height (right).

The solvent loading profiles as well as the temperature profiles for experiments with 30 wt% MEA looked different from the experiments with 30 wt% MDEA with 3.5 g/L CA. In Figure 15 the mass transfer of CO₂ over the height of the column for these two solvents is shown. The values were calculated from a material balance over the liquid phase using the solvent loading

results. The mass transfer in the enzyme enhanced solvent is much more equally distributed over the height of the column and showed a lower influence of L/G ratio. An increase in L/G ratio led to slightly higher absorption in the bottom part of the column. For a low L/G ratio 54 % of the CO₂ was capture in the top part of the column. When the L/G ratio was increased to 4.7 the value dropped to 43 % and at 6.5 L/G just 33 % of the CO₂ was captured in the upper part. The MEA solvent system was much more influence by the L/G ratio. For a low L/G ratio of 2.8 68% of the CO₂ mass transfer happened above the middle of the column. At 4.5 L/G just 33 % of the CO₂ was captured in the upper part and this value dropped even to 15 % when the L/G ratio was increased to 6.3. The reason for the higher influence of L/G ratio on the column performance is the different temperature dependency of the CO₂ mass transfer in enzyme enhanced solvents and conventional solvents like MEA. For enzyme enhanced solvent the mass transfer becomes slower when the temperature rises, whereas for MEA solution the mass transfer increases with temperature [19]. The CO₂ absorption and reaction with the solvent generates heat. In case of MEA the amount of heat is even higher than for MDEA, as the reaction between 1 mole of CO₂ and MEA releases 83 kJ of energy, whereas just around 57 kJ is released from the reaction between CO₂ and MDEA [1]. The CO₂ absorption into MEA will increase the liquid temperature and spike the mass transfer even further. This will lead to hotspots (temperature bulges) and influence the mass transfer inside the column. For enzyme enhanced MDEA the mass transfer will decrease once the temperature rises which regulates the mass transfer and prevents hot spots. It is expected that the control of an MEA process will be more difficult than an enzyme enhanced MDEA process, as small changes in L/G ratio will result in bigger changes in CO₂ capture efficiency, as seen in Figure 13, as well as temperature and loading profiles.

Figure 15: Mass transfer of CO₂ over the column height for 30 wt% MDEA with 3.5 g/L CA and 30 wt% MEA at different L/G ratios

6. Conclusion

This study clearly demonstrated how the enzyme enhanced CO₂ capture process in pilot scale benchmarks to the industrial standard solvent 30 wt% MEA. Experimental data on CO₂ capture

efficiencies, as well as solvent loading and temperature profiles inside the column are presented from 18 runs with 30 wt% MEA and 50 runs with MDEA solvents with varying CA concentrations (0, 0.85 and 3.5 g/L) at different column heights and different L/G ratios. The

The 10 m pilot absorber packed column has been characterized by experimentally determining crucial mass transfer parameters such as liquid holdup and effective mass transfer area in parallel experiments. A new method for solvent loading determination method for MDEA solutions containing CA enzyme by correlating the liquid density to the loading was introduced and validated.

The pilot absorption experiments showed a very positive effect of CA addition on the CO₂ mass transfer rate. While blank 30 wt% MDEA solvent was just capable of capturing between 18 and 23 % of the CO₂ at 10 m column height in the absorption experiments, the same solvent with 0.85 g/L CA added reached CO₂ capture efficiencies between 36 and 49 % in a similar L/G ratio range. When the CA concentration was increased to 3.5 g/L capture efficiencies as high as 48 to 83% were observed. Despite the good absorption performance of the enzyme enhanced solutions, the mass transfer of CO₂ was still lower than that of the industrial standard 30 wt% MEA. Benchmarking the different solvents showed that blank MDEA solvent without enzyme provides only around 20 % of the mass transfer performance compared to 30 wt% MEA. When 0.85 g/L CA was added the solvent was capable to capture around 50 % of the CO₂ the industrial standard captured. With 3.5 g/L CA close to 80 % of the mass transfer performance of a 30 wt% MEA solution could be reached. These observations are very encouraging for the enzyme enhanced CO₂ capture technology, since they prove that mass transfer rates can be obtained comparable to the industrial standard.

The experiments also revealed differences between MEA and enzyme enhanced MDEA solvent systems. The nature of the solvent, as well as the reaction mechanism makes MEA systems prone to temperature bulges inside the column and results column areas that are very active in the mass transfer and areas that do not participate as much. These temperature bulges and active areas can be observed also at smaller column heights and the positions are mainly influenced by the L/G ratio. Enzyme enhanced MDEA solvents did not show such behavior and it is unlikely for such a system that great temperature bulges evolve inside the column. Due to that behavior the absorption process with enzyme enhanced MDEA solvent would be easier to control than with MEA solvent system.

The gathered experimental results for the pilot campaigns can be used to derive an accurate process model for enzyme enhanced CO₂ capture.

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Appendix: Setpoints and column profiles

A) MEA campaign

Table 1: Setpoints and measured mass transfer in second MEA campaign part 1

	height	Run m	ME1 2.25	ME2 2.25	ME3 2.25	ME4 4.25	ME5 4.25	ME6 4.25	ME7 6.25	ME8 6.25	ME9 6.25
Liquid	Mass flow	kg hr ⁻¹	72.2	122.3	175.0	72.8	122.1	177.0	71.5	123.0	175.4
	T	°C	25.9	25.2	24.8	25.8	25.1	24.8	24.9	24.2	23.7
	MEA	wt%	29.5	29.5	29.5	29.5	29.5	29.5	29.2	29.2	29.2
	CO ₂	wt%	5.2	5.2	5.2	5.4	5.4	5.4	6.2	6.2	6.2
Gas	Mass flow	kg hr ⁻¹	26.5	26.2	26.2	26.4	26.5	26.6	29.2	28.4	28.7
	T	°C	22.4	22.8	23.0	23.0	23.2	23.1	24.3	26.4	24.5
	p	kPa	101.7	101.5	102.0	102.7	102.5	102.5	103.6	104.1	103.5
	CO ₂	vol%	14.1	12.4	12.4	12.8	12.7	12.6	13.1	11.8	12.1
	H ₂ O	vol%	2.7	2.7	2.8	2.7	2.8	2.8	2.9	3.3	3.0
Mass transfer CO₂		kg hr ⁻¹	2.67	2.71	2.92	3.16	3.83	4.02	3.13	3.99	4.42

Table 2: Temperature profiles in second MEA campaign part 1

height	ME1	ME2	ME3	ME4	ME5	ME6	ME7	ME8	ME9
in	25.9	25.2	24.8	25.8	25.1	24.8	24.9	24.2	23.7
10.25									
9.25									
8.25									
7.25									
6.25							28.5	25.1	24.5
5.25							46.7	28.3	26.2
4.25				30.6	25.9	25.2	51.4	31.9	28.1
3.25				48.4	31.3	28.1	50.9	37.2	31.3
2.25	31.5	27.3	25.9	56.0	40.6	32.4	46.4	45.4	36.2
1.25	47.5	36.3	31.0	50.8	48.6	36.9	41.1	47.7	40.6
0.25	35.6	35.7	32.7	35.8	41.1	36.0	29.9	33.6	34.1
0	35.1	35.9	33.5	36.3	41.4	38.0	31.4	39.7	38.4

Table 3: Loading profiles in second MEA campaign part 1

height	ME1	ME2	ME3	ME4	ME5	ME6	ME7	ME8	ME9
in	0.25	0.25	0.25	0.26	0.26	0.26	0.30	0.30	0.30
9.25									
8.25									
7.25									
6.25									
5.25							0.33	0.31	0.31
4.25							0.37	0.33	0.31
3.25							0.41	0.35	0.33
2.25							0.45	0.38	0.36
1.25							0.47	0.41	0.39
0.25							0.49	0.44	0.40
0	0.41	0.35	0.32	0.46	0.41	0.37	0.49	0.45	0.41

Table 4: Setpoints and measured mass transfer in second MEA campaign part 2

		Run	ME10	ME11	ME12	ME13	ME14	ME15	ME16	ME17	ME18
	height	m	8.25	8.25	8.25	10.25	10.25	10.25	10.25	10.25	10.25
Liquid	Mass flow	kg hr ⁻¹	75.4	123.6	176.0	49.6	75.1	99.3	126.1	150.8	175.8
	T	°C	24.9	24.2	23.8	25.8	25.0	24.5	24.2	24.0	23.9
	MEA	wt%	29.2	29.2	29.2	29.2	29.2	29.2	29.2	29.2	29.2
	CO ₂	wt%	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2
Gas	Mass flow	kg hr ⁻¹	27.6	28.3	28.4	28.3	27.2	27.4	27.7	27.7	27.8
	T	°C	26.2	25.8	24.5	26.5	28.1	26.7	23.9	23.9	24.4
	p	kPa	104.8	105.6	105.0	106.6	104.5	104.3	103.6	103.0	103.2
	CO ₂	vol%	12.2	13.1	12.5	14.4	12.1	13.3	12.6	12.1	11.6
	H ₂ O	vol%	3.3	3.2	2.9	3.3	3.7	3.4	2.9	2.9	3.0
Mass transfer CO₂		kg hr ⁻¹	3.40	4.75	5.04	2.92	3.45	4.28	4.68	4.83	4.72

Table 5: Temperature profiles in second MEA campaign part 2

height	ME10	ME11	ME12	ME13	ME14	ME15	ME16	ME17	ME18
in	24.9	24.2	23.8	25.8	25.0	24.5	24.2	24.0	23.9
10.25				36.9	34.6	28.2	23.9	23.1	23.0
9.25				48.3	48.3	38.3	26.0	24.7	24.5
8.25	38.0	24.8	23.5	51.4	58.0	53.9	27.5	25.2	24.7
7.25	63.3	28.2	24.9	49.6	61.3	67.3	35.4	26.5	25.4
6.25	63.4	31.5	25.9	45.7	58.5	66.6	57.4	28.1	26.3
5.25	59.0	43.7	28.0	41.8	54.4	63.4	68.8	32.0	28.6
4.25	56.3	60.4	30.5	39.8	51.8	61.2	68.2	37.2	30.8
3.25	52.5	64.4	33.5	38.4	48.5	57.8	65.5	44.9	33.6
2.25	48.4	62.7	38.1	36.8	44.9	54.5	62.4	55.3	37.9
1.25	42.9	56.2	42.6	33.8	40.9	48.5	55.3	55.6	42.5
0.25	29.7	38.3	38.4	29.5	33.0	35.5	40.2	40.2	37.0
0	35.7	43.1	39.8	29.7	33.6	37.7	41.7	44.4	39.1

Table 6: Loading profiles in second MEA campaign part 2

height	ME10	ME11	ME12	ME13	ME14	ME15	ME16	ME17	ME18
in	0.29	0.29	0.29	0.30	0.30	0.30	0.30	0.30	0.30
9.25				0.33	0.31	0.30	0.30	0.30	0.30
8.25				0.36	0.33	0.32	0.31	0.30	0.30
7.25	0.32	0.31	0.30	0.43	0.36	0.34	0.32	0.31	0.30
6.25	0.35	0.32	0.30	0.46	0.41	0.38	0.33	0.31	0.31
5.25	0.40	0.34	0.32	0.49	0.44	0.41	0.35	0.32	0.32
4.25	0.43	0.36	0.32	0.50	0.45	0.43	0.37	0.34	0.32
3.25	0.45	0.39	0.34	0.50	0.47	0.45	0.40	0.37	0.35
2.25	0.47	0.42	0.37	0.51	0.48	0.46	0.42	0.39	0.37
1.25	0.48	0.44	0.40	0.51	0.49	0.48	0.44	0.42	0.40
0.25	0.49	0.47	0.41	0.52	0.50	0.49	0.46	0.44	0.43
0	0.50	0.47	0.43	0.52	0.50	0.49	0.47	0.45	0.43

B) 30 wt% MDEA with 0.85 g/L CA

Table 7: Setpoints and measured mass transfer in 30 wt% MDEA 0.85 g/L CA at 10.25 m

		Run	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
	Height	m	10.25	10.25	10.25	10.25	10.25	10.25	10.25	10.25	10.25	10.25	10.25	10.25
Liquid	Mass	kg hr ⁻¹	72.7	125.1	175.8	73.2	125.1	175.7	175.6	125.7	70.8	73.3	127.0	73.0
	T	°C	28.6	28.0	28.2	40.4	39.7	39.2	25.6	26.7	28.1	39.1	37.1	39.2
	MEA	wt%	29.5	29.5	29.5	29.5	29.5	29.5	29.5	29.5	29.5	29.5	29.5	29.5
	CO ₂	wt%	2.0	2.2	2.4	3.0	3.1	3.3	3.4	3.7	3.9	0.5	0.5	3.3
	Cenz	g/L	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85
Gas	Mass	kg hr ⁻¹	22.4	22.3	22.5	21.6	21.5	21.4	21.1	21.4	21.6	20.9	20.7	22.1
	T	°C	25.6	25.6	25.4	38.4	38.0	37.7	26.7	27.2	27.7	39.1	37.1	39.2
	p	kPa	100.2	100.0	100.1	100.1	100.0	100.0	100.5	100.5	100.6	101.8	101.3	102.6
	CO ₂	vol%	13.3	12.5	13.4	12.8	12.5	12.4	13.6	13.5	13.8	13.4	12.2	13.2
	H ₂ O	vol%	3.3	3.3	3.2	6.8	6.6	6.5	3.5	3.6	3.7	6.9	6.2	6.9
Transfer CO₂		kg hr ⁻¹	1.72	1.91	2.32	0.90	1.02	1.11	1.87	1.47	0.96	1.80	2.19	1.47

Table 8: Setpoints in 30 wt% MDEA campaign with 0.85 g/L CA at different column heights

		Run	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22
	Height	m	2.25	2.25	4.25	4.25	6.25	6.25	8.25	8.25	10.25	10.25
Liquid	Mass	kg hr ⁻¹	73.3	175.4	74.9	175.3	72.4	176.5	72.7	174.2	73.7	174.7
	T	°C	25.5	24.9	26.1	25.2	26.4	25.6	26.8	26.1	27.2	26.6
	MEA	wt%	29.5	29.5	29.5	29.5	29.5	29.5	29.5	29.5	29.5	29.5
	CO ₂	wt%	0.5	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5
	Cenz	g/L	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85
Gas	Mass	kg hr ⁻¹	22.7	22.6	22.8	22.6	22.6	22.6	22.5	22.3	22.3	22.2
	T	°C	22.5	23.5	23.8	24.0	24.2	24.4	24.5	24.6	24.7	24.8
	p	kPa	99.9	99.9	100.1	99.9	100.0	99.9	100.0	100.0	99.9	99.9
	CO ₂	vol%	12.8	13.0	13.8	12.8	12.9	13.0	12.8	12.3	12.5	12.3
	H ₂ O	vol%	2.7	2.9	2.9	3.0	3.0	3.0	3.1	3.1	3.1	3.1
Transfer CO₂		kg hr ⁻¹	1.00	1.16	1.47	1.69	1.63	2.16	1.80	2.28	1.81	2.39

Table 9: Setpoints and measured mass transfer in first MDEA campaign with 0.85 g/L CA

		Run	C23	C24	C25	C26	C27	C28	C29	C30	C31	C31
	Height	m	2.25	2.25	4.25	4.25	6.25	6.25	8.25	8.25	10.25	10.25
Liquid	Mass	kg hr ⁻¹	71.4	174.8	72.9	175.3	74.2	175.7	74.6	172.7	73.2	175.7
	T	°C	39.4	40.1	41.1	41.6	41.7	41.6	41.6	40.9	40.4	39.2
	MEA	wt%	29.5	29.5	29.5	29.5	29.5	29.5	29.5	29.5	29.5	29.5
	CO ₂	wt%	2.6	2.6	2.7	2.8	2.8	2.9	2.9	3.0	3.0	3.3
	Cenz	g/L	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85
Gas	Mass	kg hr ⁻¹	22.4	22.1	21.8	21.8	21.8	21.7	21.7	21.6	21.6	21.4
	T	°C	25.6	28.5	30.2	30.8	31.4	31.8	32.0	32.2	32.4	32.3
	p	kPa	100.0	100.2	100.0	100.2	99.9	100.0	100.2	100.3	100.1	100.0
	CO ₂	vol%	12.6	13.3	12.0	13.0	12.5	12.9	13.4	12.9	13.1	12.6
	H ₂ O	vol%	3.3	3.9	4.3	4.4	4.6	4.7	4.7	4.8	4.9	4.8
Transfer CO₂		kg hr ⁻¹	0.68	0.82	0.73	0.93	0.80	1.05	0.94	1.20	0.92	1.13

C) 30 wt% MDEA with 3.5 g/L CA

Table 10: Setpoints and measured mass transfer in second MDEA campaign with 3.5 g/L CA

		Run	C32	C33	C34	C35	C36	C37	C38	C39
	Height	m	2.25	4.25	6.25	8.25	10.25	10.25	10.25	10.25
Liquid	Mass	kg hr ⁻¹	122.7	124.5	126.7	126.3	72.0	126.1	176.0	122.7
	T	°C	25.9	25.9	25.9	25.8	26.4	25.9	25.7	25.9
	MEA	wt%	31.0	31.0	31.0	31.0	31.0	31.0	31.0	31.0
	CO ₂	wt%	0.9	0.9	0.9	0.9	0.8	0.8	0.8	0.9
	Cenz	g/L	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Gas	Mass	kg hr ⁻¹	28.0	27.5	27.6	27.4	27.2	27.1	27.1	28.0
	T	°C	20.9	21.3	21.6	21.9	22.7	22.9	22.7	20.9
	p	kPa	102.8	102.4	102.9	102.6	102.8	102.1	102.4	102.8
	CO ₂	vol%	15.5	12.4	13.4	12.3	12.6	11.9	11.5	15.5
	H ₂ O	vol%	2.4	2.5	2.5	2.6	2.7	2.7	2.7	2.4
Transfer CO₂		kg hr ⁻¹	1.78	2.17	2.96	3.17	2.62	3.24	3.60	3.82

Table 11: Temperature profile in second MDEA campaign with 3.5 g/L CA

height	C32	C33	C34	C35	C36	C37	C38	C39
in	25.9	25.9	25.9	25.8	26.4	25.9	25.7	25.5
10.25					26.5	25.5	25.1	24.9
9.25					29.3	27.5	26.7	26.3
8.25				25.3	30.4	28.1	27.0	26.6
7.25				27.6	33.0	29.3	27.6	26.7
6.25			25.7	28.3	35.1	30.4	28.3	27.2
5.25			28.0	29.8	37.6	32.4	29.2	27.8
4.25		25.6	29.2	30.9	39.1	34.4	30.5	28.8
3.25		28.0	30.7	32.2	39.8	35.8	31.4	29.2
2.25	26.4	29.6	32.1	33.6	39.9	37.6	32.5	30.3
1.25	29.3	31.1	33.3	34.6	38.0	38.4	33.6	31.0
0.25	27.1	28.1	29.1	30.2	30.5	33.2	30.9	28.9
0	28.0	28.9	30.0	31.0	30.3	33.3	31.7	30.6

Table 12: Loading profile in second MDEA campaign with 3.5 g/L CA

height	C32	C33	C34	C35	C36	C37	C38	C39
in	0.08	0.08	0.08	0.07	0.07	0.07	0.07	0.04
9.25					0.10	0.08	0.08	
8.25				0.07	0.12	0.10	0.09	
7.25					0.16	0.12	0.10	
6.25			0.08		0.21	0.15	0.12	
5.25					0.25	0.18	0.14	
4.25		0.08			0.28	0.20	0.16	
3.25					0.30	0.22	0.18	
2.25	0.08				0.33	0.26	0.22	
1.25					0.35	0.29	0.24	
0.25					0.38	0.31	0.26	
0	0.20	0.24	0.29	0.31	0.39	0.32	0.27	0.22

Table 13: Setpoints and measured mass transfer in second MDEA campaign with 3.5 g/L CA

		Run	C40	C41	C42	C43	C44	C45	C46
	Height	m	2.25	4.25	6.25	8.25	10.25	10.25	10.25
Liquid	Mass	kg hr ⁻¹	123.9	122.5	124.6	123.5	72.1	124.0	175.8
	T	°C	28.7	28.7	28.7	28.7	27.7	27.6	28.0
	MEA	wt%	31.0	31.0	31.0	31.0	31.0	31.0	31.0
	CO ₂	wt%	2.5	2.5	2.5	2.5	2.5	2.5	2.5
	Cenz	g/L	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Gas	Mass	kg hr ⁻¹	28.0	27.6	27.5	27.6	27.7	27.4	27.4
	T	°C	22.1	22.5	23.0	23.4	24.1	24.3	24.1
	p	kPa	102.2	102.1	102.2	102.5	101.9	101.3	102.3
	CO ₂	vol%	13.4	11.9	11.9	12.4	14.3	12.5	11.9
	H ₂ O	vol%	2.6	2.7	2.7	2.8	2.9	3.0	2.9
Transfer CO₂		kg hr ⁻¹	1.21	1.60	2.06	2.34	1.99	2.43	2.77

Table 14: Temperature profile in second MDEA campaign with 3.5 g/L CA

height	C40	C41	C42	C43	C44	C45	C46
in	28.7	28.7	28.7	28.7	27.7	27.6	28.0
10.25					28.3	27.4	27.1
9.25					31.0	29.2	29.0
8.25				28.1	32.1	29.8	29.4
7.25				30.1	33.9	30.8	29.8
6.25			28.5	30.7	35.1	31.9	30.4
5.25			30.3	31.7	36.2	33.3	31.2
4.25		28.2	31.5	32.6	36.7	34.6	32.1
3.25		30.5	32.3	33.3	36.8	35.3	32.6
2.25	28.8	31.9	33.5	34.3	36.7	36.4	33.6
1.25	31.1	32.5	33.8	34.3	35.2	36.2	33.8
0.25	28.6	29.6	30.5	30.9	30.1	32.3	31.5
0	28.7	29.5	30.3	30.7	29.7	31.8	31.6

Table 15: Loading profile in second MDEA campaign with 3.5 g/L CA

run	C40	C41	C42	C43	C44	C45	C46
height	2.25	4.25	6.25	8.25	10.25	10.25	10.25
in	0.22	0.22	0.22	0.22	0.22	0.22	0.22
0	0.30	0.34	0.35	0.33	0.42	0.37	0.35

D) Capture efficiencies for the different solvent systems

Table 16: Comparison of capture efficiencies of 30 wt% MEA to 30 wt% MDEA with varying enzyme concentrations the different solvents at column heights between 2 and 8 m

Solvent	Loading (mol/mol)	T (°C)	L/G (kg/kg)	2.25 m	4.25 m	6.25 m	8.25 m
30 wt% MEA		28	3.2	45%	60%	52%	65%
30 wt% MEA	0.24 (2-4 m)	28	5.4	53%	74%	77%	85%
30 wt% MEA	0.29 (6-8 m)	28	7.8	58%	79%	84%	95%
30 wt% MDEA 0.85 g/L CA	0.1	28	4.0	21%	29%	35%	39%
30 wt% MDEA 0.85 g/L CA	0.1	28	9.6	24%	36%	46%	53%
30 wt% MDEA 0.85 g/L CA	0.27	40	4.0	16%	18%	19%	20%
30 wt% MDEA 0.85 g/L CA	0.27	40	9.6	18%	21%	24%	27%
30 wt% MDEA 3.5 g/L CA	0.07	28	4.5	25%	40%	51%	60%
30 wt% MDEA 3.5 g/L CA	0.22	28	4.5	20%	31%	38%	43%

Table 17: Comparison of capture efficiencies of 30 wt% MEA and 30 wt% MDEA with varying enzyme concentrations for different L/G ratios at a column height of 10.25 m

Solvent	Loading (mol/mol)	T (°C)	L/G 2.1	L/G 2.6	L/G 3.3	L/G 4	L/G 4.5	L/G 5.5	L/G 6.5	L/G 7.6	L/G 9.5
30 wt% MEA	0.29	28	46%		68%		77%	89%	97%	98%	
0 g/L CA	0.05	28			18%			20%		23%	
0.85 g/L CA	0.1	28				40%					56%
0.85 g/L CA	0.27	40				20%					26%
3.5 g/L CA	0.07	28		48%			65%		75%		83%
3.5 g/L CA	0.22	28		32%			44%				54%

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