Development of a Spray Scrubbing Process for Post Combustion CO₂ Capture with Amine Based Solvents

Oliver Seyboth, Simone Zimmermann, Barna Heidel*, Günter Scheffknecht

Institute of Combustion and Power Plant Technology (IFK)
University of Stuttgart, Pfaffenwaldring 23, 70569 Stuttgart, Germany

Abstract
The application of a spray tower for CO₂ capture instead of a packed absorber column promises substantial advantages, such as reduction of investment and operating costs due to the omission of expensive packing and an insignificant pressure drop. Additionally, a spray scrubbing process offers the opportunity to use precipitating solvents. Moreover, a much higher flexibility of the process towards load changes is expected, because there is no packing that has to be permanently wetted, and no close fluid-dynamical limitations exist for the gas and liquid flow rate. In order to demonstrate the applicability of a spray scrubbing process for CO₂ capture and to investigate the most important process and design parameters, a two-way experimental approach was chosen. In laboratory scale experiments, the kinetics of CO₂ absorption by single solvent droplets was measured for variations of the process parameters CO₂ partial pressure, solvent loading and droplet size. Additionally, a prototype spray scrubber plant designed for treating up to 150 m³ N/h raw gas was put into operation for testing the closed loop absorption – desorption process.

Keywords: CO₂ capture, CCS, amine scrubbing, spray scrubbing

* Corresponding author. Tel.: +49-711-685 68946; fax: +49-711-685 63491.
E-mail address: barna.heidel@ifk.uni-stuttgart.de
1. Introduction

Great effort is currently put into the development of CO$_2$ capture and storage technologies (CCS) for fossil fuel-fired power plants in order to minimize greenhouse gas emissions from power generation. One of the most mature capture technologies is a chemical scrubbing process with amine based solvents which can also be applied for retrofitting existing power plants. In this process, a chemical solvent is brought into contact with the flue gas in an absorption column where it absorbs the CO$_2$ from the gas phase. Typically, the absorption column is packed with a random or structured packing which provides a large surface area for mass transfer. However, improvements of the process concerning energy- and cost-efficiency and its flexibility towards load changes are still crucial for large-scale application. The application of a spray tower instead of a packed absorber column promises substantial advantages: investment and operating costs could be reduced due to the omission of expensive packing and a very low pressure drop. Additionally, a spray scrubbing process offers the opportunity to use precipitating solvents based on amino acid salts which are currently under development [1]. Moreover, a much higher flexibility of the process towards load changes is expected because there is no packing that has to be permanently wetted and no close fluid-dynamical limitations exist for the gas and liquid flow rate.

Despite its promising features, very few studies concerning a spray scrubbing process for CO$_2$ capture with amine-based solvents have been published so far. Kuntz and Aroonwilas [2] compared the CO$_2$ capture performance of a spray scrubber to that of a packed absorber column by the determination of overall mass transfer coefficients from laboratory scale experiments. They found a very promising CO$_2$ capture performance of the spray scrubber with overall mass transfer coefficients significantly higher than for the packed column. Koller et al. [3] published results from a larger pilot spray scrubber plant where up to 160 m$_3$/h of raw gas can be treated. Unlike Kuntz and Aroonwilas, they found the measured absorption performance was not sufficient for a large scale application. In both studies, mass transfer was determined by measuring inlet and outlet gas or liquid concentrations while very small spray columns of only 0.1 and 0.15 m in diameter were applied. For this reason, absorption by the spray cannot be quantified separately from absorption by the liquid film on the inner column wall, during droplet formation and at the column sump. Additionally, the size of spray droplets, defining the interfacial surface area as well as the liquid side mass transfer coefficient and the droplets velocity of fall are not specified in these studies.

In order to demonstrate the applicability of a spray scrubbing process for CO$_2$ capture and to identify and investigate the most important process and design parameters, a two-way experimental approach was applied in this study. In laboratory scale experiments, the absorption of CO$_2$ by single droplets of the solvent spray is investigated in detail. The rate of CO$_2$ absorption is measured while the most important process parameters, such as CO$_2$ partial pressure, solvent loading and droplet size are varied. Additionally, the overall closed-loop spray scrubbing process consisting of spray scrubbing and solvent regeneration was tested in a newly constructed pilot plant. For all experiments presented here, a 30 weight-% solution of Monoethanolamine (MEA) was used as a solvent. With its primary amino group, MEA is able to directly react with CO$_2$ forming a carbamate-ion with a stable molecular bond. The carbamate-formation is a very fast reaction, enhancing mass transfer of CO$_2$ from gas to liquid phase significantly. In a much slower parallel reaction, CO$_2$ is bound in solution as bicarbonate. For primary amines, the carbamate formation is the dominant absorption mechanism [4] leading to high mass transfer rates at low CO$_2$ solvent loading.

2. Experimental

For the investigation of the absorption of CO$_2$ by single falling spray droplets, a new laboratory-scale experimental setup was developed. This setup allows the measurement of the rate of CO$_2$ absorption at a constant temperature by droplets of different sizes within the technically relevant range for CO$_2$ gas concentration. In order to test the overall closed-loop CO$_2$ capture process with spray scrubbing and subsequent regeneration and reuse of the solvent, a pilot plant capable of treating 150 m$_3$/h of raw gas was constructed.
2.1. \( \text{CO}_2 \) absorption by single spray droplets

The experimental setup constructed to investigate the absorption of \( \text{CO}_2 \) by single falling droplets is schematically shown in Fig. 1. The absorption takes place in a vertical double walled acrylic glass cylinder with an inner diameter of 34 mm and a height of 2.5 m. This absorber is operated at atmospheric pressure while its temperature is controlled with water via an external thermostat. The solvent is pumped continuously through a temperature controlled oil bath to the top of the absorber where single droplets are formed at the end of a capillary. When a droplet reaches its critical weight defined by the surface tension of the solvent and the diameter of the capillary, it falls down through the absorber which is filled with a mixture of \( \text{CO}_2 \) and \( \text{N}_2 \). At the bottom, the droplets are collected with a funnel and led into an external container via a siphon. The funnel as well as the space around the capillary are flushed with a minimum flow of \( \text{N}_2 \), just sufficient to prevent absorption during droplet formation and collection. The absorber is flushed with a continuous flow of \( \text{CO}_2 \) and \( \text{N}_2 \) which is sufficient to maintain a constant gas concentration but only leading to a negligible gas flow velocity. Absorption of \( \text{CO}_2 \) takes place only while the drop is falling from the absorber top to bottom. This time of fall \( t_c \) can be calculated by the law of falling bodies.

![Experimental setup for absorption by single droplets](image)

The droplet generation mechanism guarantees the formation of drops with uniform size. For experiments with different droplet sizes, different capillaries of appropriate diameters were used. The minimum droplet diameter \( d_{\text{drop}} \) in this experimental setup turned out to be approximately 3.0 mm. Smaller droplets tend to hit the column wall due to small disturbances in the gas flow. In order to investigate the influence of the \( \text{CO}_2 \) solvent loading on the rate of absorption, 30 wt.-% MEA with different initial loading was used in the experiments. Therefore, the solution was preloaded with pure \( \text{CO}_2 \) up to the intended loading. Two gas flow controllers are used to supply \( \text{CO}_2 \) and \( \text{N}_2 \) which also enable a variation of the gas composition. All experiments were carried out at a temperature of 40 °C. In Table 1, an overview of the experimental process parameters investigated in this study is given.
Table 1. Process parameters for single droplet experiments

| Parameter                      | Value                        |
|-------------------------------|------------------------------|
| Solvent                       | 30 wt.-% MEA                 |
| Temperature                   | 40 °C                        |
| Drop size                     | \(d_{\text{drop}} = 3.1 / 4.1 / 4.5 \text{ mm}\) |
| Initial solvent loading       | \(\alpha = 0.15 / 0.25 / 0.35 / 0.45 \text{ mol}_{\text{CO}_2}/\text{mol}_{\text{amine}}\) |
| CO₂ gas concentration         | 2.5 / 5.0 / 10 / 15 vol.-%   |

The rate of CO₂ absorption \(r_{\text{abs}}\) is defined according to eq. (1) as the increase in solvent loading \(\Delta \alpha\) per unit time of contact between the gas and falling droplet. Therefore, after each experiment the initial CO₂ loading of the solvent feed is analysed as well as the loading of the collected droplets sample. CO₂ loadings are determined by expelling all CO₂ from the solvent sample by addition of a surplus of hydrochloric acid. The weight loss due to degassing of CO₂ is recorded with a precision balance.

\[
r_{\text{abs}} = \frac{\Delta \alpha}{t_c}
\]  

\(2.2.\) Spray scrubber pilot-plant

In Fig. 2, a schematic of the closed-loop spray scrubber pilot-plant is shown. The plant was designed for the treatment of up to 150 m³/h of an artificial flue gas which is mixed from CO₂ and N₂. The absorption takes place within an array of three consecutive polypropylene spray towers, each 5 m high and with an inner diameter of 0.37 m. While the raw gas is entering absorber 1 at the bottom and leaving absorber 3 at the top, the solvent spray is directed in a countercurrent flow through the spray towers. Therefore, the solvent with lean CO₂ loading is sprayed at the top into absorber 3, collected at the bottom and sprayed into absorber 2 before it is finally sprayed into absorber 1. At the bottom of absorber 1 the solvent has reached rich loading. From there, it is pumped via a cross flow heat exchanger to the desorber were it is regenerated by stripping off the absorbed CO₂. The desorber consists of a stainless steel column with random packing and an electrically heated reboiler. Its height is 3 m and its inner diameter 0.3 m. The regenerated solvent is pumped via the cross flow heat exchanger back to the top of absorber 3 and reused for absorption.

The CO₂ released in the desorber is remixed with the clean gas between the water washing section and the demister following the spray columns. Approximately 95% of the overall gas flow is recycled to the inlet of absorber 1. The remaining 5% are discarded through the chimney in order to maintain a constant raw gas composition by adding CO₂ and N₂ with automatically regulated mass flow controllers (MFC).
Fig. 2. Spray scrubber pilot-plant

A special feature of the pilot-plant is the splitting of the spray tower into three segments with a single full cone spray nozzle at the top of each one. This setup guarantees, despite the small column diameter, that only a minimum portion of the solvent spray hits the inner column wall before it is collected in the sump and atomized again at the top of the next absorber. Furthermore, a staged solvent sampling and additional intercooling of the solvent during absorption are possible. Different spray nozzles can be installed in the spray towers in order to investigate the influence of spray cone geometry and droplet size distribution on the process.

The pilot-plant is equipped with multiple sampling points and instrumentation which allow to determine gas concentration and temperature profiles, as well as pressure drops and the energy demand for regeneration. For the determination of concentration profiles over the spray tower height, sampling points are integrated at the top, middle and bottom of each absorber. At these points, the CO₂ concentration can be measured with infra-red gas analyzers. With consecutive concentration measurements at all sampling points in steady state operation, an overall profile over the cumulative spray tower height of the three absorbers is generated. The overall removal efficiency can be calculated from the inlet and outlet CO₂ concentrations, \( y_{\text{CO}_2,\text{inlet}} \) and \( y_{\text{CO}_2,\text{outlet}} \), by the following equation:

\[
\text{Removal efficiency} = \frac{y_{\text{CO}_2,\text{inlet}} - y_{\text{CO}_2,\text{outlet}}}{y_{\text{CO}_2,\text{inlet}}} \times 100\% \quad (2)
\]

Liquid samples are taken from the sumps of the absorbers as well as from lean solvent. From the liquid samples, the CO₂ solvent loading is determined as described for the laboratory scale experiments. Additionally, the amine concentration is determined by acidic titration in order to monitor the water balance.

In Table 2, the process parameters for the pilot-plant experiments are shown. The raw gas flow rate was 120 m³/h with a CO₂ content of 15 vol.-%. Full cone spray nozzles with a spray angle of 90° were installed. From the
manufacturers information with the applied solvent flow rate of 590 l/h, a sauter mean diameter of $d_{\text{Sauter}} = 1.6 \text{ mm}$ can be assumed. The solvent flow rate was defined by the assumption that absorption of 90\% of the CO$_2$ should lead to an increase of the solvent loading by 0.25 mol$_{\text{CO$_2$/mol_amine}}$. For the overall capture process, a lean solvent loading of 0.2 mol$_{\text{CO$_2$/mol_amine}}$ and a rich loading of 0.45 mol$_{\text{CO$_2$/mol_amine}}$ were assumed. However, the height of the three consecutive spray columns is not sufficient for a removal efficiency of 90\%. Therefore, the overall process was simulated by three consecutive operating points (A), (B) and (C).

### Table 2. Process parameters for pilot-plant experiments

| Operating Point | (A) | (B) | (C) |
|-----------------|-----|-----|-----|
| Solvent        | 30 wt.-% MEA | 30 wt.-% MEA | 30 wt.-% MEA |
| Nozzle          | Full cone spray nozzle, Lechler GmbH Type 461.086.17/90° | 1.6 | |
| $d_{\text{Sauter}}$ [mm] | 1.6 | |
| Raw gas flow rate [m$^3$/h] | 120 | 590 | 120 |
| $y_{\text{CO$_2$/inlet}}$ [vol.-\%] | 15 | 12.9 | 8 |
| Solvent flow rate [l/h] | 590 | |
| $\alpha_{\text{rich}}$ [mol$_{\text{CO$_2$/mol_amine}}$] | 0.45 | 0.4 | 0.3 |
| $T_{\text{Absorber}}$ [°C] | 40 | |
| $T_{\text{Desorber}}$ [°C] | 120 | |
| $p_{\text{Desorber}}$ [bar] | 2 | |

For the first operating point (A), the overall raw gas concentration of 15 vol.-\% was defined as the inlet gas concentration. The reboiler heat supply was iteratively adjusted to a value resulting in a rich solvent loading of 0.45 mol$_{\text{CO$_2$/mol_amine}}$. Operating point (A) is, therefore, representing the bottom part of the overall spray scrubbing process where the raw gas gets into contact with the maximum loaded solvent. Results from operating point (A) are a clean gas concentration of 12.9 vol.-\% after the third absorber and a lean solvent loading of 0.4 mol$_{\text{CO$_2$/mol_amine}}$. These values are used as the input parameters for inlet gas concentration and rich solvent loading for operating point (B) in the same way as described for point (A). Finally, the resulting clean gas concentration of 8 vol.-\% CO$_2$ and the lean solvent loading of 0.3 mol$_{\text{CO$_2$/mol_amine}}$ from (B) are used as input parameters for the third operating point (C). Operating points (B) and (C) are, therefore, representing the middle and upper part of the overall spray absorption process. By combination of the operating points, continuous profiles of gas concentration and solvent loading for the overall process can be obtained as a function of the cumulative spray tower height.

### 3. Results and Discussion

In Fig. 3 and 4, results from laboratory scale experiments are shown. In Fig. 4, the rates of absorption for droplets of 4.1 mm are depicted as functions of the solvent loading at different CO$_2$ gas concentrations. For any gas concentration, $r_{\text{abs}}$ must be zero for the respective equilibrium solvent loading. These data points are taken from separate equilibrium measurements and shown in the graph together with the measured absorption rates.
With increasing solvent loading, \( r_{abs} \) decreases as well as with a decrease of CO\(_2\) concentration in the gas phase. This behaviour can easily be explained when a physical model for the absorption mass transfer, e.g. the two film theory, is applied to describe \( r_{abs} \) in accordance with the definition of eq. (1). From the resulting mass transfer equation (3) it is obvious that in the first approximation, \( r_{abs} \) is proportional to the driving force \((p_{CO2} - p_{CO2}^{eq})\). As the equilibrium CO\(_2\) partial pressure \( p_{CO2}^{eq} \) is increasing with increasing solvent loading, \( r_{abs} \) must be reduced in this case as well as with a decrease of the actual CO\(_2\) partial pressure \( p_{CO2} \).

\[
r_{abs} = K_{ov} \cdot \left(p_{CO2} - p_{CO2}^{eq}\right) \cdot \frac{M_{MEA}}{\rho_{solvent} \cdot x_{MEA}} \cdot \frac{A_{drop}}{V_{drop}}
\]

The overall mass transfer coefficient, \( K_{ov} \), accounts for all physical transport phenomena. It describes the influence of fluid properties like viscosities, diffusion coefficients, as well as the impact of flow pattern and the enhancement of mass transfer by a chemical reaction. Therefore, \( K_{ov} \) is also affected by an increase solvent loading because fluid properties change as well as the concentration of free amine molecules available for reaction with CO\(_2\). The molar weight \( M_{MEA} \), mole fraction \( x_{MEA} \) of MEA and the density of the solvent \( \rho_{solvent} \) are required to relate the amount of absorbed CO\(_2\) to the number of MEA molecules within a droplet of the volume \( V_{drop} \). The surface area \( A_{drop} \) of the droplet is the interfacial surface area available for mass transfer. In Fig. 4, \( r_{abs} \) is shown for a) \( d_{drop} = 4.6 \) mm and b) \( d_{drop} = 3.2 \) mm, both in comparison to \( d_{drop} = 4.1 \) mm. As expected, \( r_{abs} \) is significantly lower for large droplets and higher for small droplets. Although \( r_{abs} \) is proportional to the quotient \( V_{drop} / A_{drop} \), its dependency on \( d_{drop}^{-1} \) is not linear because \( K_{ov} \) is also affected by the droplet size. Fluid dynamic phenomena like internal circulation and oscillation of the droplet are dependent on \( d_{drop} \) and strongly affect the liquid side mass transfer resistance [5,6].
With a number of simplifying assumptions, the measured rates of CO₂ absorption can be used for an estimation of the required height of the spray tower for a full size spray scrubbing process. With a defined CO₂ raw gas concentration, a demanded CO₂ removal efficiency, and defined rich and lean solvent loadings, the profile of corresponding gas- and liquid concentrations is defined for the whole absorber. By interpolation between the measured values of \( r_{\text{abs}} \) according to this concentration profile, the required time of contact between gas and drops can be calculated for small increments of solvent loading. From the overall time of contact, the required height has to be calculated by the law of falling bodies, taking into account the flow resistance due to the gas flow upwards through the absorber. In Fig. 5 the resulting relative spray tower height is shown for the three experimental droplet sizes.

Assumptions of a raw gas concentration of 15 vol.-% of CO₂, a CO₂ removal efficiency of 90%, and rich and lean solvent loadings of 0.45 and 0.2 mol CO₂/mol amine, are taken respectively. Furthermore, the gas flow rate upwards through the absorber was assumed at 3 m/s. From Fig. 5 it becomes clear that the required height is strongly dependent on the size of spray droplets. Thereby, the effect of smaller droplet size is positive in two ways: first, the required time of contact is reduced because of the increased interfacial surface area, second, the velocity of fall is significantly lower which is reducing the required height for the same time of contact. The optimum droplet size for a large scale process is expected to be within the range of \( d_{\text{drop}} = 1-2 \) mm. In this range, a required spray tower height of less than 40 m can be expected, while the energy demand for solvent atomization is still moderate and the risk of droplet entrainment by the gas flow is still low.
Results from pilot-plant operation are shown in Fig. 6 and 7. In Fig. 6, the measured gas concentration and solvent loading are depicted as a function of the cumulative spray tower height according to the gas flow through the three absorbers. At the height of 0 m, the raw gas with 15 vol.-% CO₂ is entering absorber 1 at the bottom. After the third absorber, at a height of 15 m, a clean gas concentration of 12.9 vol.-% is reached. The lean solvent is entering absorber 3 at a height of 15 m with a loading of 0.4 mol CO₂/mol amine. At the bottom of absorber 1 the intended rich loading of 0.45 mol is reached. Absorption within the sump of each column has been taken into account by a correction of the cumulative spray tower height with respect to the geometrical sampling point positions. From the concentration gradients within the adjacent column sections, the height required for the absorption observed within the sump was estimated and added to the geometrical height.

In Fig. 7, the results from operating points (B) and (C) are depicted in the same way. With a clean gas concentration of 4 vol.-% of CO₂, a removal efficiency of 90% is not fully reached after the third operating point (C). An additional operating point would be required to complete the simulation of the overall capture process. However, from the concentration gradient of operating point (C) it can be concluded that another 5 to 10 m of spray tower height would be sufficient to achieve a removal efficiency of 90% CO₂. The overall required spray tower height would, then, be approximately 55 m.

In Fig. 8, the overall absorption process is depicted by a combination of the operating points (A), (B) and (C). Both profiles, gas concentration and solvent loading, are continuous over the cumulative spray tower height. From
that observation it can be concluded that boundary effects at the spray nozzles and due to wetting of the column wall are negligible in comparison to the spray absorption. From the profiles in Fig. 7, it becomes apparent that in the middle part of a hypothetical full size spray tower, the highest absorption rates take place. This finding is in well accordance with the results from the laboratory scale experiments. From Fig. 3 and 4 it is clear that the highest rates of CO\textsubscript{2} absorption in a capture process are present in a region with moderate CO\textsubscript{2} loadings but where still a high CO\textsubscript{2} gas concentration is present. Towards the top of the absorber, the mass transfer rate is limited by the low gas concentration despite the lean solvent loading. Towards the bottom of the absorber, the mass transfer rate is limited by the high solvent loading which prohibits an enhancement by chemical reaction.

![Fig. 8. Cumulative profiles of gas concentration and solvent loading (A) + (B) + (C)](image)

Although the results from pilot plant operation clearly confirm a very good separation efficiency of the spray scrubbing process, it becomes apparent that the observed mass transfer efficiency is lower than predicted by the laboratory scale experiments. With only 0.3 m/s, the gas flow velocity within the pilot-plant spray towers is much lower than the 3 m/s assumed for a large scale process. When 0.3 m/s are assumed, and using an extrapolation of the experimental droplet sizes for \(d_{\text{Sauter}} = 1.6\) mm according to Fig. 5, the required spray tower height following the from laboratory scale experiments lies within the range of 40 to 50 m. The fact that, with approximately 55 m, a higher spray tower is required according to the pilot-plant results, can be explained by spray droplets hitting the inner absorber wall as well as by the distribution of droplet sizes in the spray. Solvent droplets hitting the column wall are forming a liquid film with a reduced interfacial surface area. Also, effects like coagulation of spray droplets reduce the interfacial surface area, and are, thus, limiting the overall observed mass transfer efficiency.

4. Conclusions

A two-way experimental approach was applied to demonstrate the applicability of a spray scrubbing process for CO\textsubscript{2} capture and to investigate the most important process parameters. A laboratory scale experimental setup was developed to investigate the absorption of CO\textsubscript{2} by single spray droplets. The rate of CO\textsubscript{2} absorption was measured within the technically relevant range of CO\textsubscript{2} gas concentration and solvent loading. Furthermore, the influence of droplet size on the absorption rate was investigated. By using the experimental data for an estimation of the required spray tower height, it was shown that the absorption kinetics are clearly sufficient for an industrial scale capture process. While the effect of all process parameters on \(r_{\text{abs}}\) was well in accordance with theoretical consideration, it became apparent that sufficiently small spray droplets are crucial for the process. From the results and further considerations, an optimum droplet size of \(d_{\text{drop}} = 1-2\) mm is concluded. The overall spray scrubbing process, comprising a closed-loop of spray absorption and solvent regeneration, was tested in a newly constructed pilot plant treating 120 m\textsubscript{3}/h of raw gas. Results from the pilot plant confirm the applicability of spray absorption technology for CO\textsubscript{2} capture. Mass transfer efficiency observed in pilot-plant operation was approximately 10 to 20% lower than
predicted from the laboratory scale experiments. This can be explained by the wetting of the inner column wall and by the distribution of spray droplet sizes in the pilot plant.

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