Project no. 608535

INTERACT

INnovaTive Enzymes and polyionic-liquids based membRAnes as CO_2 Capture Technology

Deliverable 4.1:

Report on benchmarking tests and standardized experimental procedures of the absorption/desorption in column technology

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PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	X

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Summary

This deliverable aims to show the validation not only of the used mass absorption equipment itself but also the measurement procedures. Benchmarking of wetted wall column experiments at DTU and at facilities of the twinning partner CSIRO (Coal-AUS) by a personnel exchange from TUDO have been carried out. Experimental setup as well as the experimental procedure is comparable, which results in a high accordance of the results achieved for CO2 absorption in 30 wt.-% MEA.

In the next step the technical scale absorption equipment in terms of packed absorption columns is benchmarked. Therefore, first of all the experimental procedure and setup of TUDO is benchmarked against a column of an inner diameter of 600 mm, which is the basis for a standardized method for mass transfer measurements in absorption. A good accordance could be shown in terms of hydrodynamics and mass transfer, whereas a slight influence of the column diameter was detected. For the final benchmarking experiments comparing the column at DTU and TUDO, slight adjustments of the column setup at DTU are carried out. These experiments are about to be conducted within the next months.

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1. Benchmark experiments: Wetted Wall Column

The experiments in the wetted wall column give the mass transfer coefficients independent of the packed absorption column necessary for modelling of enzyme accelerated reactive absorption processes. Therefore, a benchmark of this type of equipment was carried out.

1.1. Experimental setup

The wetted wall columns at DTU and at the facilities of the twinning partner CSIRO (Coal-AUS) have been investigated. For the experiments at CSIRO (Coal-AUS) a personnel exchange from TUDO has been carried out within the twinning activities.

1.1.1. DTU

The wetted wall column is a gas-liquid contactor that allows carrying out mass transfer experiments at very well defined process conditions. This setup consists of two different systems, the liquid system and the gas system that get in contact in the wetted wall chamber. Inside this chamber the liquid is flowing down a small metal pipe in contact with the upstreaming gas stream. From all the auxiliary equipment it is possible to set the desired process conditions very precisely and conduct steady state experiments.

The liquid system (the blue part of Figure 1) works with a closed liquid loop and a big liquid reservoir ensuring no change in CO_2 concentration in the liquid during experiments. The liquid is pumped from the tank through a heat exchanger to heat up the solvent to the desired reactor temperature and then to the wetted wall column, the flow rate can be monitored on a rotameter. The liquid then enters the chamber from the bottom by rising up inside the small metal pipe, and then it flows down by gravitational force resulting in a ripple free film. From a correlation of a free falling liquid film running down a vertical plate the film thickness can be estimated. It can be seen from Figure 2, that the actual contact area between the gas and liquid is higher than the sole dimensions of the pipe, as the liquid film thickness needs to be accounted for. From the high liquid to gas ratio inside the reaction chamber it can be assumed that the CO_2 concentration in the liquid does not change inside the wetted wall, as the amount of absorbed CO_2 is small compared to the liquid flow. The liquid is collected at the bottom and then pumped back into the liquid reservoir.

The gas system (the red part of Figure 1) is an open system. This gas stream is pumped through two saturators, one at ambient temperature and the other at reactor temperature, to ensure saturation of the gas stream. This gas stream can now be led either through the wetted wall column or through the bypass. Independently which way the gas follows the gas temperature and CO_2 concentration are measured.

The absorption flux is measured by a component balance over the gas stream. The gas is first set on bypass mode and all process condition, including CO_2 concentration are taken down, the gas stream is then passed through the wetted wall column and the new CO_2 is measured in the gas stream. The absorption flux is calculated from that CO_2 concentration difference.

$$\Delta N_{CO2} = \frac{N_{Inert} \times (y_{CO2in} - y_{CO2out})}{(1 - y_{CO2in}) \times (1 - y_{CO2out})} \tag{1.1}$$

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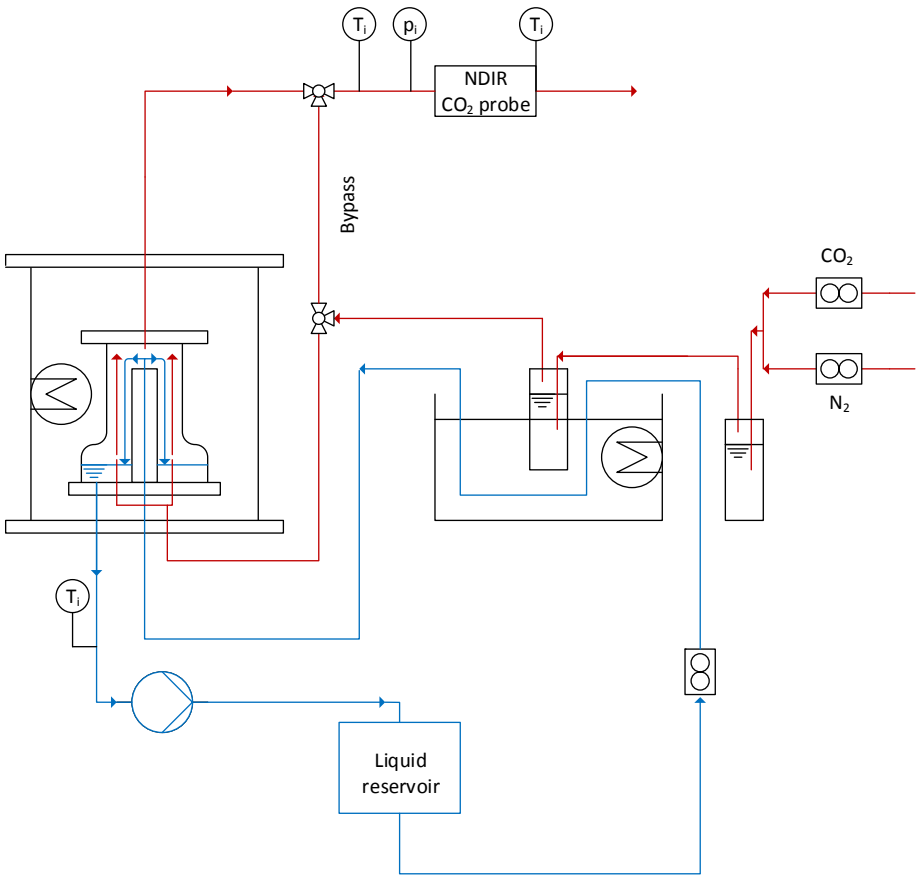

Figure 1: Wetted wall column setup, liquid system in blue colour and gas system in red colour

Table 1: Equipment on wetted wall column

Device	description	specification
Mass flow controller	EL-FLOW from Bronkhorst	0-20 nl/min N_2 and 0-2 nl/min CO_2
CO_2 probe	Vaisala	0-20 vol % at ambient conditions
Liquid flowmeter	Sho-rate rotameter	Non corrosive sapphire ball
Wetted wall chamber	Custom built	See dimensions in next figure

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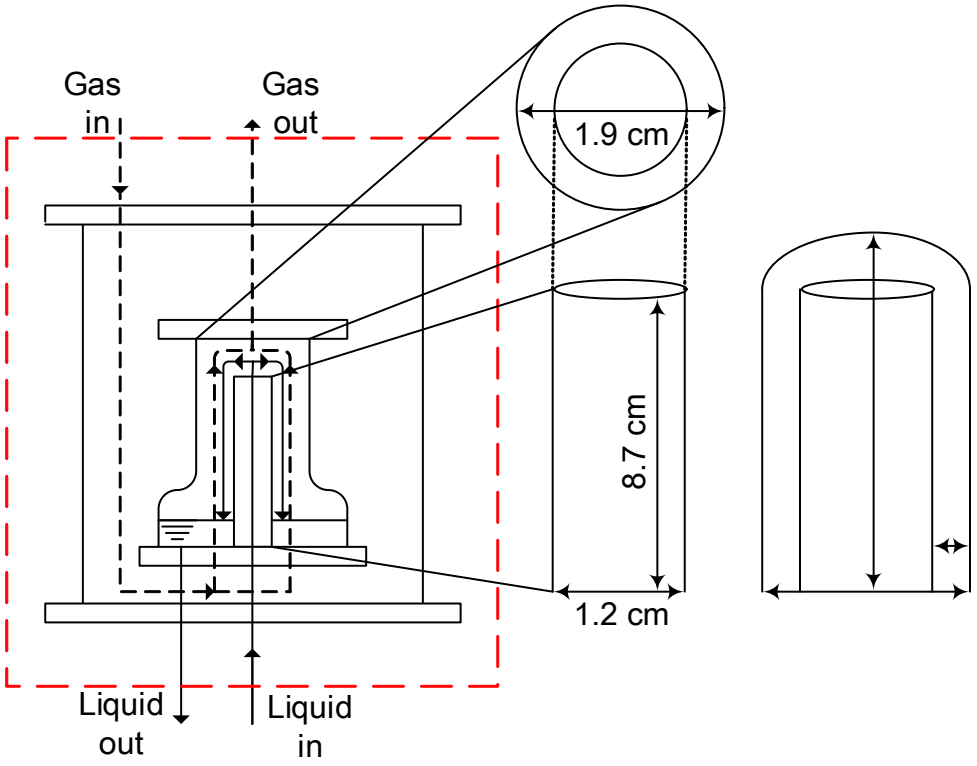

Figure 2: Scheme and dimensions of the wetted wall column at DTU

1.1.2. TUDO at CSIRO

The core of the equipment used at the twinning partner CSIRO consists of wetted wall column (WWC), which is surrounded by a heating jacket to realize isothermal conditions for the mass transfer measurements. CO_2 and N_2 are mixed in volume fractions between 4 – 20 vol.- % and are saturated with water before entering the wetted wall column at the bottom. Preheated solvent runs in counter current mode. The inlet and outlet CO_2 concentrations are measured with a gas analyser to determine the absorbed amount of CO_2. Table 2 describes the details of the applied equipment.

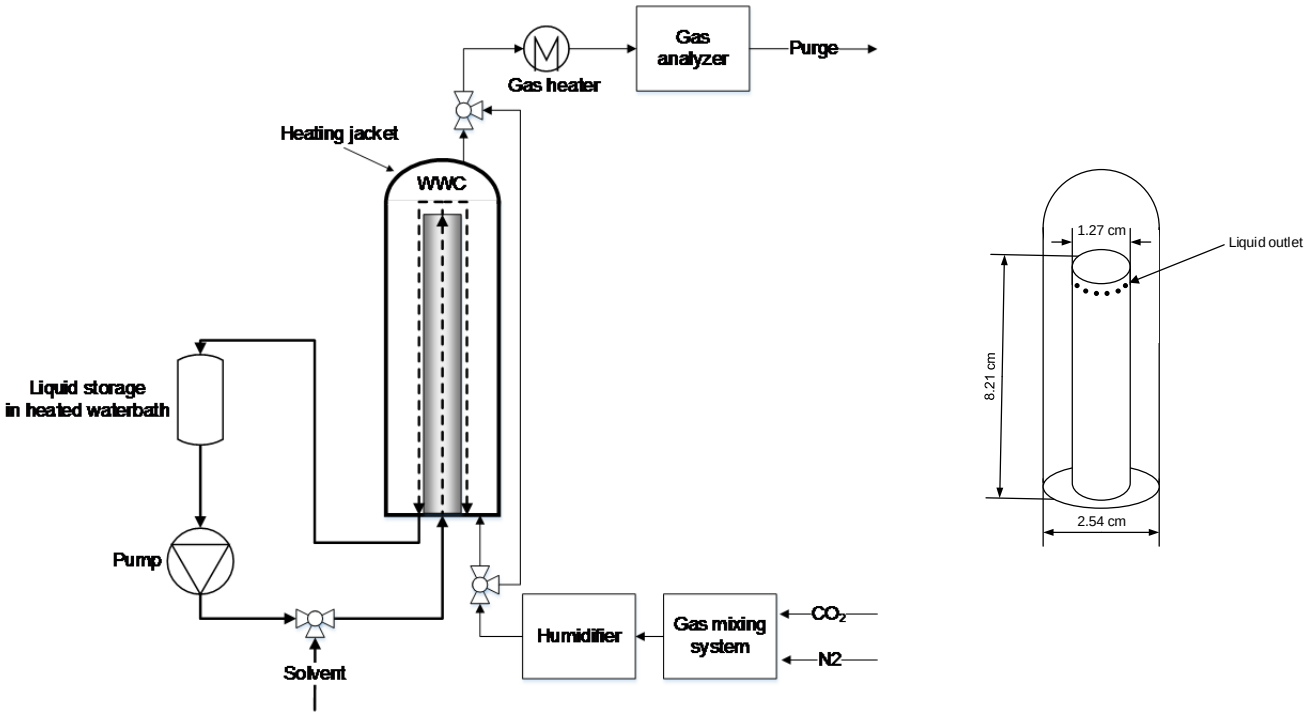

Figure 3: Setup of the wetted wall column at CSIRO used by TUDO for the benchmarking experiments

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Table 2: Equipment on wetted wall column

Device	description	specification
Mass flow controller	Bronkhorst	0-20 nl/min N_2 and 0-2 nl/min CO_2
CO_2 probe	Horiba VA 3000	0-20 vol % at ambient conditions
Wetted wall chamber	Custom built	See dimensions in next figure

1.2. Experimental procedure

The absorption experiments were conducted at similar conditions. The liquid flow was pumped in a closed loop; the mass flux as well as the solvent temperature was observed. The gas stream was set with the mass flow controller to result in a total gas stream of 3 nl/min. This stream was then bubbled through a pre saturator and saturator containing water at the process temperature to ensure saturation. This gas stream was first bypassed and the CO_2 concentration was checked, when the concentration was stable the valve was switched and the gas stream was led through the wetted wall column and the decrease in CO_2 concentration was measured. After all process parameter stabilized, the gas stream was set into bypass mode again and a different CO_2 concentration was set with the mass flow controller. Working with the same total gas stream in all experiments allows better comparison, as the gas velocity influences the gas side mass transfer. The gas and the liquid stream met inside the WWC; the liquid flows down a pipe creating a thin liquid film, and the gas stream enters in 3 gas inlets in bottom and gets in contact with the liquid film while streaming upwards.

From the well-known dimensions of the pipe and correlation for the film thickness it is possible to determine kinetics of the absorption.

1.3. Mass transfer experiments 30 wt.-% MEA

Benchmarking mass transfer measurements in both columns were carried out and the molar CO_2 flux N_{CO2} was determined over the driving force Δp_{CO2}. Figure 4 shows that the slopes of the measurements carried out at DTU and carried out at the twinning partner at CSIRO by TUDO are in good accordance. Therewith, a successful benchmarking of the mass transfer measurements in lab scale wetted wall columns can be stated.

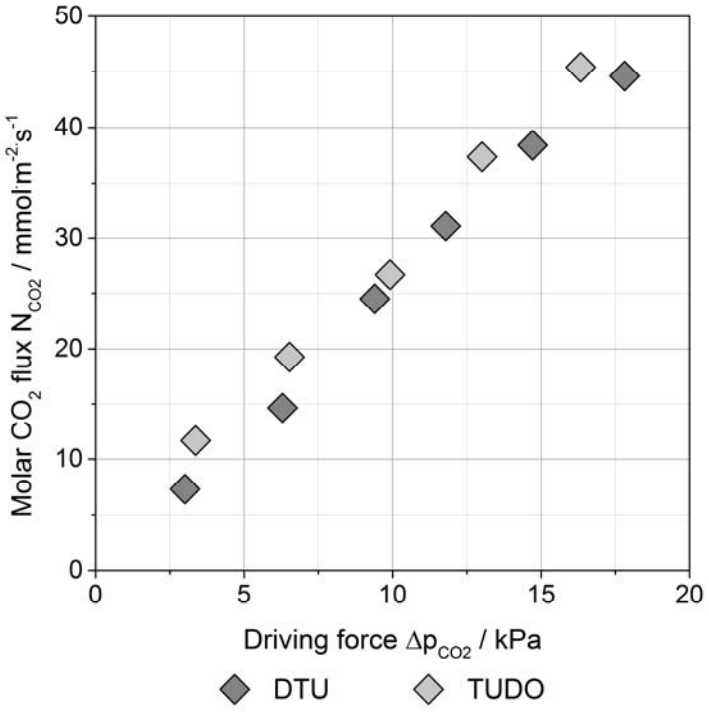

Figure 4: Molar flux vs. driving force given for 30 wt.-% MEA at $T_{solvent}$ = 313 K

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2. Benchmark experiments: Packed column

The following chapter describes the experimental setup and procedure of the absorption miniplant, which is used for the benchmarking experiments carried out within INTERACT. This method is based on common practice guidelines of mass transfer measurements in mini and pilot plant scale [1,2].

2.1. Experimental setup

In the following the packed absorption plants are described. For the bechmarking experiments for both columns an inner diameter of approx. 100 mm was chosen to be able to carry out experiments with the same packing material was used (Mellapak 250.Y by sulzer Chemtech Ltd.). This is due to the fact that the columns are additionally benchmarked against a column with an inner diameter of 600 mm, which is the basis for a standardized method for mass transfer measurements in absorption columns [1,2].

2.1.1. TUDO

For the benchmarking experiments, a packed column with an inner diameter of 110 mm was chosen to offer a good comparability to the plant at DTU. For the first experiments using carbonic anhydrase accelerated solvent the packing section of the column is changed to a diameter of 56 mm to be able to run the absorption miniplant with lower liquid volume flows to reduce the amount of enzyme spent for each experiment. A simplified flowsheet is given in **Figure 5** and details of the column setup are shown in Table 3. For the benchmark experiments the humidifier and the absorption column are used. The gas stream is presaturated to minimize the evaporation of the solvent in the absorption column. Both columns are run in countercurrent mode. Gas concentration at the absorption column inlet and outlet of the absorption column as well as temperatures and volume flows of gas and liquid streams are recorded. The solvent is passing the absorption column once and is transferred to the loaded liquid storage tank afterwards.

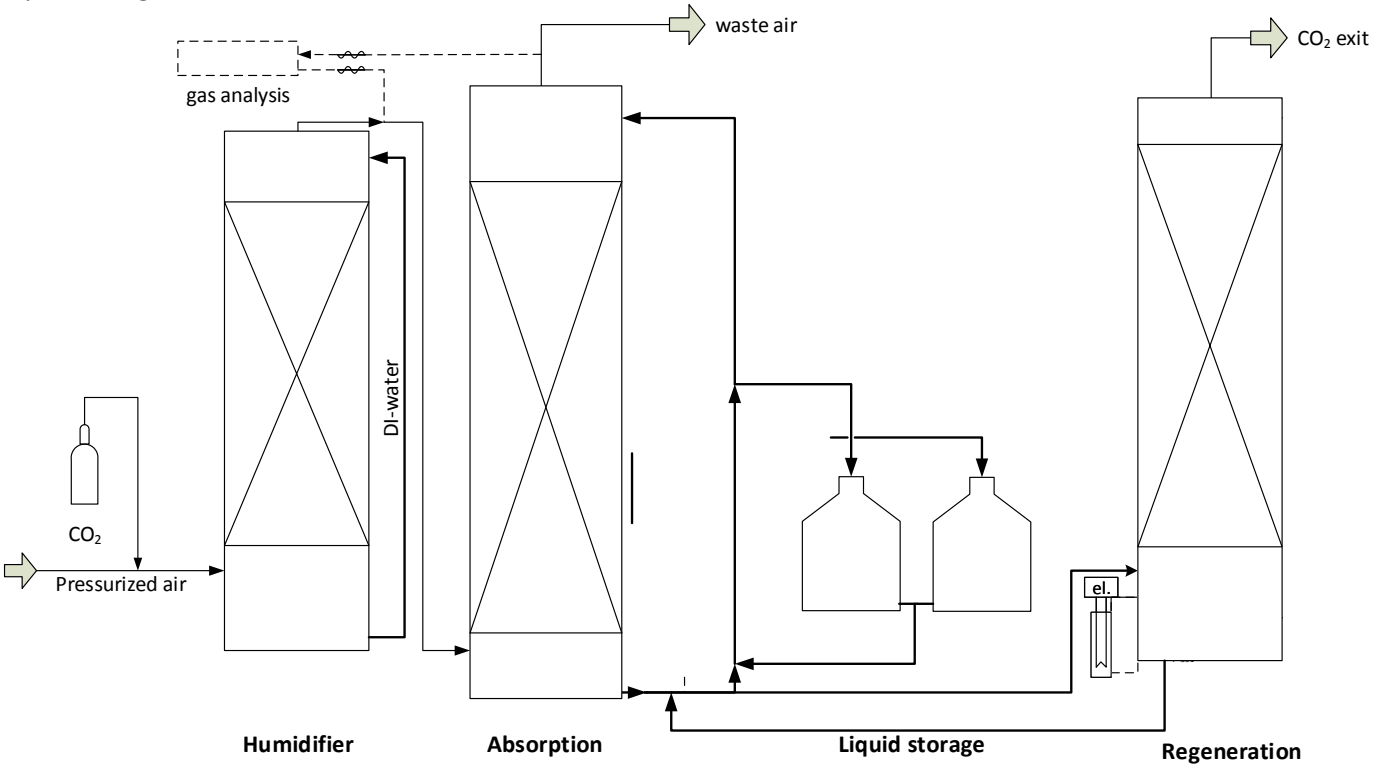

Figure 5: Simplified flowsheet of the absorption miniplant (TUDO)

Table 3: Configuration of the absorption miniplant (TUDO)

Type	Specification
Diameter	D_i=110 mm

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Packing	Mellapak 250.Y by Sulzer Chemtech Ltd.	
Packing height		H=2.3 m
Operating mode	Countercurrent	
Gas distributor	Pipe down Distance to packing < 100 mm	D_{Pipe}=2.50 mm
Liquid distributor	Pipe distributor Distance to packing approx. 350 mm	842 drip points/m²
Sampling	Gas analyzer: Liquid samples:	Above and beyond the packing

2.1.2. DTU

The setup of the absorption pilot facility can be seen in Figure 6. It has a total height of 10 m and an inner diameter of 10 cm and is filled with the structured Packing Mellapak 250 Y. Each meter a temperature probe for the liquid side and a possibility to draw a liquid sample is installed. There are 5 different liquid inlets in 2 m intervals making it possible to run the column with a shorter height between 2 to 10 m. The liquid is pumped from one big storage tank through the column and then collected in the next storage tank. The gas system in this setup is working in a closed loop. The gas is agitated by a big fan; in operating mode CO_2 is added from a bottle which is situated on a scale. Therewith, the amount of CO_2 that is added to the system is measured. The closed gas loop makes a presaturator unnecessary as the circulating gas is saturated in water and solvent for the process temperature.

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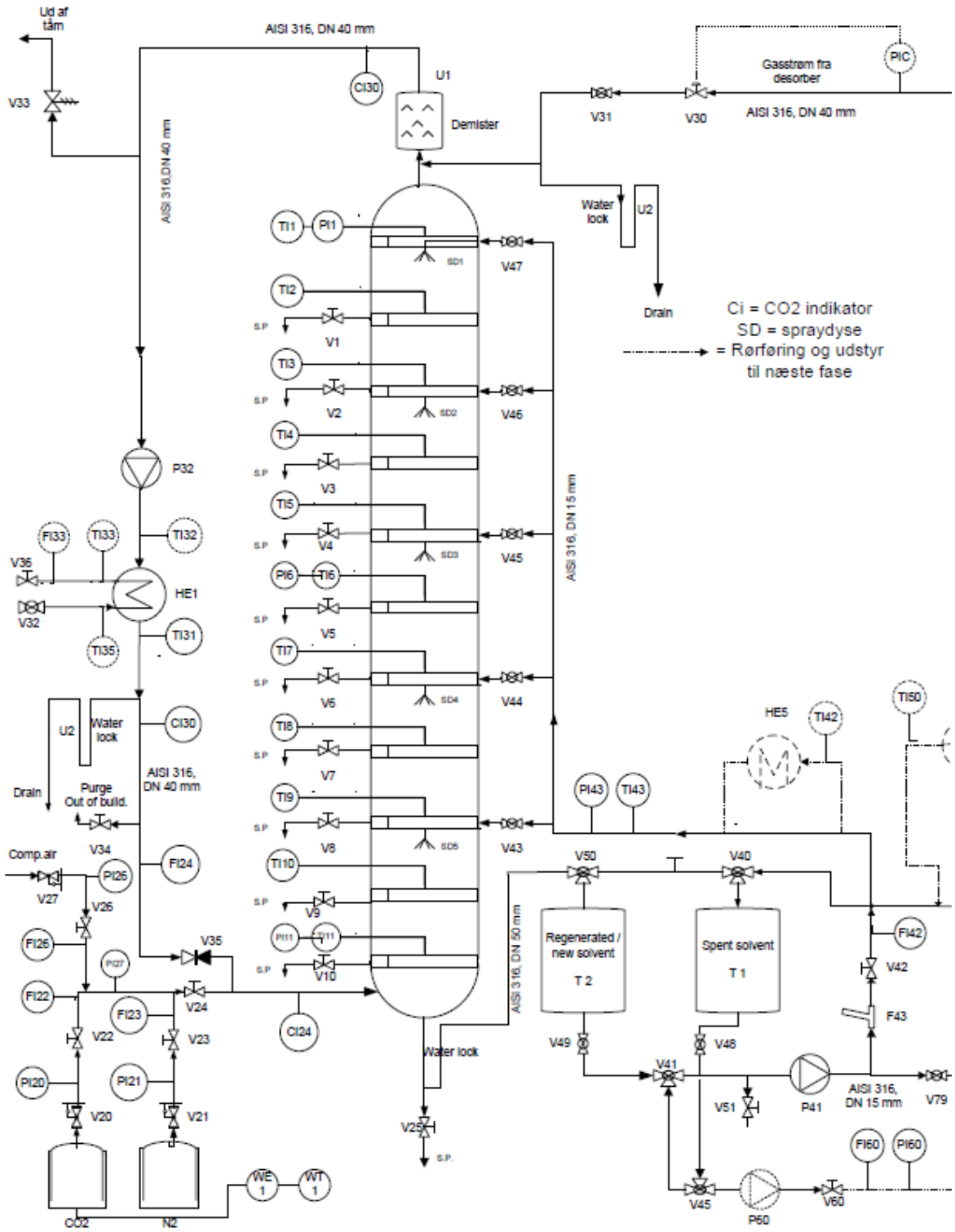

Figure 6: Flowsheet of the absorption pilot plant at DTU

Table 4: Configuration of the absorption miniplant (DTU)

	Type	Specification
Diameter		0.1 m
Packing	Sulzer Mellapak 250 Y	
Packing height		10 m total with 8.2 m packing
Operating mode	Countercurrent, with closed gas loop	

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Gas distributor	
Liquid distributor	Every 2 m redistribution of liquid, and possible liquid inlet
Sampling	Liquid sampling possible every 1m height of the column (0.82 m packing)→ $BaCl_2$ method Gas analyzer at the gas inlet and gas outlet

2.2. Standardized experimental procedure

In the following section the experimental procedure is described and a transfer of this method from TUDO to DTU has been realized by a personnel exchange of a DTU researcher to take part in experiments carried out at TUDO.

2.2.1. Data processing

The evaluation of mass transfer measurements is not only based on raw data, but also on processed data to achieve a comparative database of the experimental data.
To be able to compare experimental results in different column dimensions, the volume flows of gas and liquid are normalized. The liquid volume flow is referred to the cross sectional area of the column.

$$u_L = \frac{\dot{V}_l}{A_k} \tag{2.1}$$

Due to the high temperature dependency of gas, the gas volume flow is not only referred to the cross section of the column, but also to the density of the gas, which results in the gas load factor, which is commonly called the F-Factor F_V.

$$F_V = \frac{\dot{V}_G}{A_k} \cdot \sqrt{\rho_G} \tag{2.2}$$

Based on those values the fluid dynamics of a column are characterized. Key values are the liquid hold-up and the dry as well as the wet pressure drop. They define the loading as well as flooding range of a column.
Liquid hold-up h_L defines the amount of liquid within the packing during operation. This can be divided into the static hold-up that occurs due to the adhesion force of the packing. In contrast to that, the dynamic hold-up is dependent on the liquid volume flow.

2.2.2. Hydrodynamics

An accurate determination of mass transfer in absorption columns needs a determination of the hydrodynamics in the column. This is especially interesting for the distribution of the liquid in the column and the residence time. All these parameters influence on the removal rate of the chemical absorption.
When a column is operated beyond the loading point, the ratio between gas and liquid stream is characterized by a constant level of liquid hold-up in the column referred to the gas stream. It depends only on the liquid load. Beyond the loading point the liquid hold-up is increasing with the gas load up to the flooding point, where it reaches its maximum value.
Dry pressure drop represents the gas side pressure drop within a packed column, where only gas is flowing without any liquid contact.
Wet pressure drop represents the pressure drop within a packed column, where gas and liquid are contacted.
Below the loading point the slopes of dry and wet pressure drop are parallel, as there is no interference between liquid and gas stream. Above the loading point the liquid hold-up represents an additional resistance for the gas flow. Therewith, the wet pressure drop beyond the loading point is sharper. The region where the slope is close to vertical is called the flooding range. In this range the gas flow is so high, that the liquid cannot flow down the column anymore and is spilling on top of the packing.

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Hydrodynamics are normally measured at 7 different F-Factors F_V for 5 different liquid loads u_L and additionally the dry pressure drop, which equals a (u_L = 0 $m^{3}{\cdot}m^{-2}{\cdot}h^{-1}$). Time till hydrodynamic steady state operation is reached has to be determined in advance.

1. Measurement of pressure drop and hold up (u_L > 0 $m^{3}{\cdot}m^{-2}{\cdot}h^{-1}$)
   a) Start the humidifier with a constant liquid flow.
   b) Start the inlet and outlet pumps and adjust the highest possible liquid load.
   c) Start the ventilator (inlet) and adjust the highest gas load to realize an operation in the flooding region to ensure an adequate wetting of the packing. Retain this operating condition for at least 2-3 minutes. At this time, a tightness and function test of the test facility can be completed.
   d) Beginning of the actual measurements by the adjustment of the liquid load. The liquid flow must be constant for this measurement series.
   e) Adjust the targeted gas load in the column.
   f) Adjust of the liquid level in the sump to a constant level.
   g) After the adjustment of the gas and liquid flow, the operation conditions have to reach steady state. Steady operation conditions are reached with constant pressure drops, temperatures and liquid level in sump.
   h) Pressure drop and temperatures are recorded when steady state is reached
   i) Liquid level in the sump is recorded.
   j) Measurement of the hold up: Shut down of liquid pumps and ventilator and closing of all valves of the inlet and outlet pipes to the column simultaneously.
   k) Wait till maximum increase in liquid level is reached. The necessary time is plant and packing specific and should be determined in advance
   l) Recording the increase of the liquid level ΔH in the sump to determine specific hold up h_L
   m) Repeat step c) – k) for all 7 gas and 5 liquid loads by increasing the flows. To ensure hydrodynamic results over the whole operating range of the packings, the last two points of measurements should be at the loading respectively flooding point.

2.2.3. Mass transfer measurements

Mass transfer measurement should be carried for at least 5 different F-Factors F_V for different liquid loads u_L in the operating window of the absorption column. For mass transfer measurements the stepwise procedure looks as follows. Reproducibility with a maximum deviation between each measurement of ±20% in the concentrations of the gas and liquid phase is targeted.

2. Mass transfer measurements:
   a) Start the gas analyser
   b) Check the sampling devices for the liquid probes (tightness, function, possible contamination).
   c) Carry out step 1a) to 1e)
   d) Introduce the gas component into the gas inlet.
   e) Record of the pressure drops.
   f) Record of the gas inlet and outlet concentration and volume flows after gas inlet and outlet concentration and temperatures show a constant value (±20 ppm for the given setup). The necessary time for constant inlet and outlet concentrations of the gas component is plant specific and should be determined in advance.
   g) Take liquid samples
      - Rinse sampling device and sample flask
      - Fill flask completely to minimize gas volume in the flask to avoid gas liquid contact
   h) Repeat step 2a) – 2g) for all gas and liquid loads.

Hydrodynamic measurements

The hydrodynamic behavior of the system is applied using water and air. Key values of the hydrodynamics are the dry and irrigated pressure drop as well as the liquid hold-up in the packing.

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Mass transfer measurements

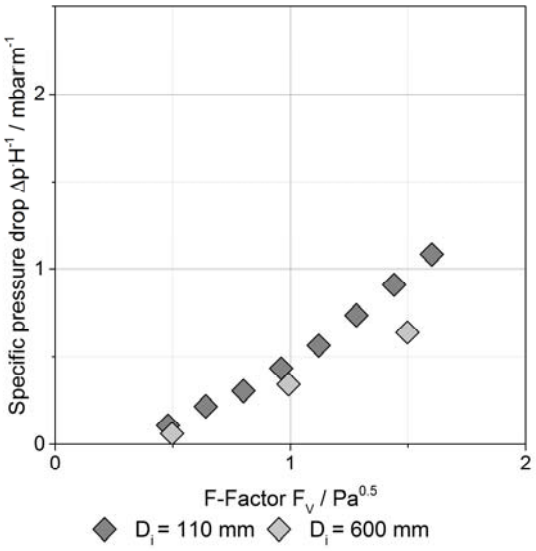
Table 5: Chemical system under investigation

Gas Phase	Liquid phase
CO_2 - Air	1 M NaOH

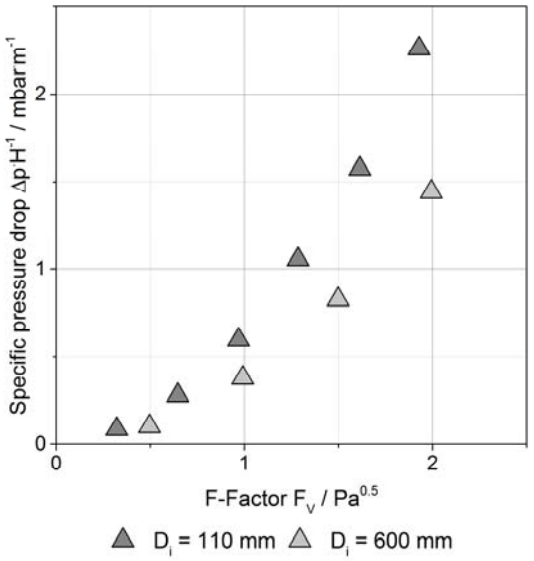
2.3. Results

In the following section, results of comparative measurements with the packed column at TUDO (Di=110 mm and

2.3.1. Hydrodynamics



u_L = 0 $m^3 \cdot m^{-2} \cdot h^{-1}$



u_L = 20 $m^3 \cdot m^{-2} \cdot h^{-1}$

Figure 7Figure 7 shows the dry (u_L = 0 $m^{3} \cdot m^{-2} \cdot h^{-1}$) and irrigated ($u_L$ = 20 $m^{3} \cdot m^{-2} \cdot h^{-1}$) pressure drop for the two investigated columns. The pressure drop for the smaller column, which is part of this project, is higher due to the wall friction, as expected. But in general pressure drop curves show a comparable slope and therewith a successful hydrodynamic benchmarking can be stated here.

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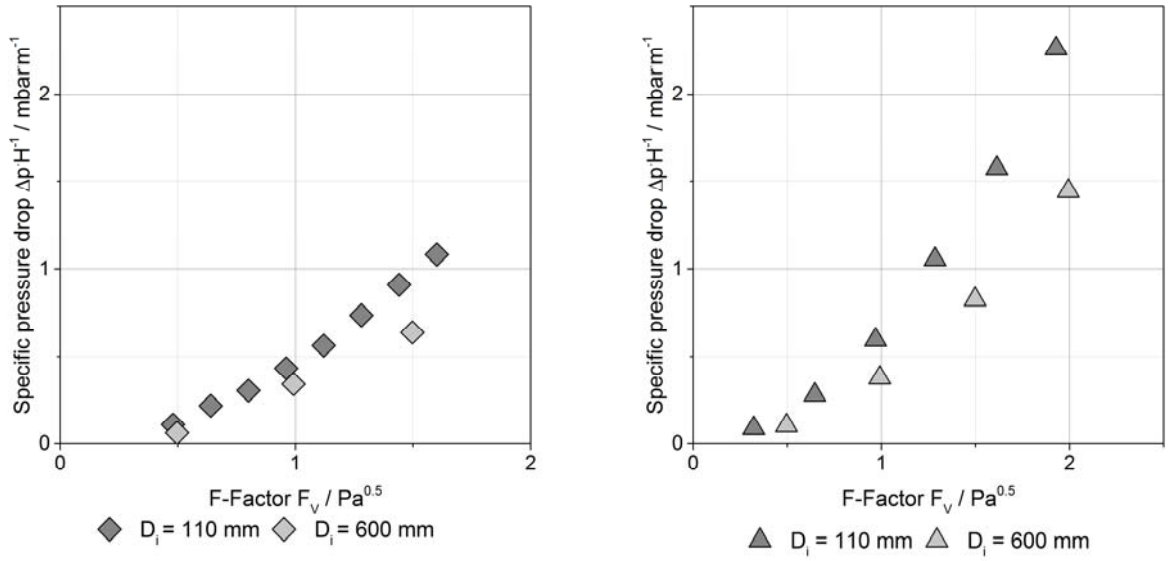

u_L = 0 $m^3 \cdot m^{-2} \cdot h^{-1}$ u_L = 20 $m^3 \cdot m^{-2} \cdot h^{-1}$

Figure 7: Specific pressure drop for two different column diameters (Mellapak 250.Y) dependent of the specific liquid load u_L for a constant F-Factor F_V 1.5 $Pa^{0.5}$ at $T_{ambient}$ = 293 K and $p_{ambient}$ = 1 bar K

2.3.2. Mass transfer

Figure 8 shows the results of the volumetric overall mass transfer coefficient $K_G a_{eff}$ measured in the absorption column at TUDO in comparison to the results based on the standardized method. The results of the measurements carried out in the D_i = 110 mm column show an increase of the volumetric overall mass transfer coefficient $K_G a_{eff}$ for low specific liquid loads. This is probably due to unequal liquid distribution at lower liquid loads. But Figure 8 shows that for liquid loads u_L > 20 $m^3 \cdot m^{-2} \cdot h^{-1}$ the determined volumetric overall mass transfer coefficient $K_G a_{eff}$ are in a comparable range like the measurements in the column with a higher column diameter (D_i = 600 mm). Therewith, a successful benchmarking of the packed column has been shown.

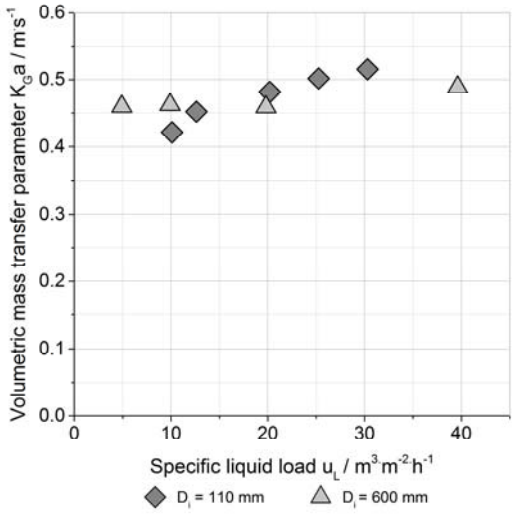

Figure 8: Volumetric overall mass transfer coefficient $K_G a_{eff}$ for two different column diameters (Mellapak 250.Y) dependent of the specific liquid load u_L for a constant F-Factor F_V 1.5 $Pa^{0.5}$ at $T_{ambient}$ = 293 K and $p_{ambient}$ = 1 bar

In a last step of benchmarking, the achieved results for the packed column at TUDO have to be compared to the results of DTU in the next months.

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3. References

[1] **Kunze, A.-K., Lutze, P., Schoenmakers, H.**, et al., Die Notwendigkeit einer Standardisierung von Stofftransportmessungen in der Ab- und Desorption, *Chemie Ingenieur Technik **84** (11)*, pp. 1931–1938 (2012).

[2] **Hoffmann, A., Maćkowiak, J.F., Górak, A.**, et al., Standardization of Mass Transfer Measurements: A Basis for the Description of Absorption Processes, *Chemical Engineering Research and Design **85** (1)*, pp. 40–49 (2007).

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